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(54) 【発明の名称】 吸湿性架橋アクリル系繊維及び該繊維を用いた繊維構造体

## (57) 【要約】

【目的】 吸放湿速度が制御された調湿調湿性高吸湿繊維であって、pH緩衝性、難燃性、抗菌性、消臭性、抗ビル性、制電性、保水性、水吸上げ性、乾燥のし易さ等の調和機能を合わせ有する、健康・快適・安全・衛生及びイージーケア性を備えた繊維を提供する。

【構成】 20℃65%RHに於ける飽和吸湿率が1.5～3.5重量%であって、下記速度式の吸湿速度定数 $k_1$ が0.015～0.029の範囲で且つ放湿速度定数 $k_2$ が0.005～0.015の範囲である調湿・調湿機能を有することを特徴とする吸湿性架橋アクリル系繊維。  
 $W_1 = W_0 \cdot (1 - e^{-k_1 t})$ 、 $W_1$  : 絶乾から時間 $t$ における吸湿率、 $W_0$  : 20℃65%RH飽和吸湿率、 $k_1$  : 吸湿速度定数、 $t$  : 0～30分、 $W_2 = (W_a - W_b) \cdot (1 - e^{-k_2 t})$ 、 $W_2$  :  $W_b$  から時間 $t$ における吸湿率、 $W_a$  : 20℃30%RH飽和吸湿率、 $W_b$  : 20℃80%RH飽和吸湿率、 $k_2$  : 放湿速度定数、 $t$  : 0～30分

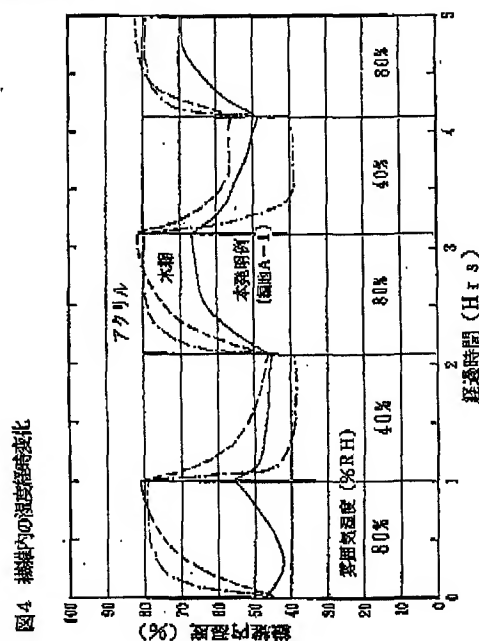


図4 繊維中の水分量変化

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## 【特許請求の範囲】

【請求項1】 20℃65%RHに於ける飽和吸湿率が15～35重量%であって、下記速度式の吸湿速度定数 $k_1$ が0.015～0.029の範囲で且つ放湿速度定数 $k_2$ が0.005～0.015の範囲である調湿・調湿機能を有することを特徴とする吸湿性架橋アクリル系繊維。

$$W_1 = W_s (1 - e^{-k_1 t})$$

$W_1$  : 絶乾から時間 $t$ における吸湿率

$W_s$  : 20℃65%RH飽和吸湿率

$k_1$  : 吸湿速度定数

$t$  : 0～30分

$$W_2 = (W_s - W_b)(1 - e^{-k_2 t})$$

$W_2$  :  $W_b$  から時間 $t$ における吸湿率

$W_s$  : 20℃30%RH飽和吸湿率

$W_b$  : 20℃80%RH飽和吸湿率

$k_2$  : 放湿速度定数

$t$  : 0～30分

【請求項2】 pH緩衝性、難燃性、抗菌性、消臭性、抗ビル性、制電性、吸水性、及び乾燥のし易さの調湿機能をさらに有することを特徴とする請求項1記載の吸湿性架橋アクリル系繊維。

【請求項3】 アクリル繊維にヒドラジン処理により架橋構造を導入して窒素含有量の増加を1.0～8.0重量%の範囲内に調整し、加水分解により残存しているニトリル基量の1.0～5.0meq/gにカルボキシル基を、残部にアミド基を導入し、次いで該カルボキシル基の50～90mol%をMg, Ca, Cu, Zn, Al, Ag, Feより選ばれる1種あるいは2種以上の金属塩型とする吸湿性架橋アクリル系繊維であって、最終熱処理の乾熱温度を100～230℃で行なうことを特徴とする請求項1又は2記載の吸湿性架橋アクリル系繊維。

【請求項4】 請求項1～3のいずれかに記載の吸湿性架橋アクリル系繊維を10wt%以上含有してなることを特徴とする繊維構造体。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は吸・放湿速度が制御された調湿・調湿機能を有する高吸湿性繊維であって、pH緩衝性、難燃性、抗菌性、消臭性、抗ビル性、制電性、保水性、水吸上げ性、乾燥のし易さなどの調湿機能を合わせ有する、健康・快適・安全・衛生及びイージーケア性を備えた吸湿性架橋アクリル系繊維に関する。また本発明は該繊維を含有する繊維構造体に関するものであり、該構造体を利用した製品は上記の機能によって快適な生活環境の提供に寄与するものである。

## 【0002】

【従来の技術】気密化、暖冷房化などの生活環境の変化、高齢化及び生活文化の高度化の時代に適応し得る健

康・快適・安全・衛生機能を合わせ持つ高機能複合素材が期待されている。これに対応して人体機能と着心地性に関する繊維製品消費科学研究の進展は著しい。身体からは絶えず水分が蒸発しており、暑熱時、運動時や通気性の低い衣服や寝具を着用した時には発汗し、衣服内・寝具内の温度が高くなり、むれ感を生じる。一方、吸湿率に乏しい衣服や吸湿率が高くて吸湿・放湿速度が速い衣服を着用した場合には、冷暖房室内への出入り等の環境変化に対して、冷感や暑感を生じやすい。又、このような寝具を着用した場合には保温性に乏しいか、保温性はあってもむれ感や早朝の冷感などの不快感を経験することは良く知られている。吸湿性繊維としては、木綿、羊毛などの天然繊維、再生繊維のレーヨン、半合成繊維のアセテート等が使用される。一方、吸湿性の乏しい合成繊維の場合は、近年技術の進歩によって微細な空洞や溝を有する繊維が出現し、従来の合成繊維の欠点を補う工夫がなされてきた(例えば、特開昭57-51812, 特開平03-161506)。しかしながら、これらの繊維は水吸上げ速度や保水性に優れるものの吸湿率が乏しいために、衣服内の温湿度を調整する機能を十分満足するものではなかった。

【0003】一方、空気中の湿気を取り再生可能な吸湿・放湿性架橋アクリル系繊維(特開平5-132585)が提案され、その20℃65%RHでの飽和吸湿率は最大55%の実施例が示されており、吸放湿速度が速いことが特徴として謳われている。この繊維は吸着熱による発熱や脱湿能力に優れているが、吸湿能力、脱湿能力が高すぎることから、人体と接する衣服や寝具に使用される場合には、皮膚表面の保温性が失われる欠点が予測される。

## 【0004】

【発明が解決しようとする課題】本発明はかかる従来技術の問題点を解消するために創案されたものであり、その目的とするところは衣服内の温湿度を適度に調節する調湿・調湿機能を持つ吸湿性架橋アクリル系繊維を提供することにある。更に、本発明の目的はpH緩衝性、難燃性、抗菌性、消臭性、抗ビル性、制電性、保水性、水吸上げ性、乾燥のし易さなどの調湿機能を合わせ有する、健康・快適・安全・衛生及びイージーケア性を備えた吸湿性架橋アクリル系繊維並びに該繊維を含有する繊維構造体を提供することにある。

## 【0005】

【課題を解決するための手段】本発明は上記目的を達成するために鋭意検討した結果、本発明の完成に至った。即ち、本発明は20℃65%RHに於ける飽和吸湿率が15～35重量%であって、下記速度式の吸湿速度定数 $k_1$ が0.015～0.029の範囲で且つ放湿速度定数 $k_2$ が0.005～0.015の範囲である調湿・調湿機能を有することを特徴とする吸湿性架橋アクリル系繊維である。

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$$W_1 = W_0 (1 - e^{-k_1 t})$$

$W_1$  : 絶乾から時間 $t$ における吸湿率

$W_0$  : 20℃65%RH飽和吸湿率

$k_1$  : 吸湿速度定数

$t$  : 0~30分

$$W_2 = (W_a - W_b)(1 - e^{-k_2 t})$$

$W_2$  :  $W_b$  から時間 $t$ における吸湿率

$W_a$  : 20℃30%RH飽和吸湿率

$W_b$  : 20℃80%RH飽和吸湿率

$k_2$  : 放湿速度定数

$t$  : 0~30分

【0006】また、本発明の吸湿性架橋アクリル系繊維は上記調湿・調湿機能に加えて、pH緩衝性、難燃性、抗菌性、消臭性、抗ビル性、制電性、吸水性、及び乾燥のし易さの調和機能をさらに有する。

【0007】上記の諸機能を有する吸湿性架橋アクリル系繊維はアクリル繊維にヒドラジン処理により架橋構造を導入して窒素含有量の増加を1.0~8.0重量%の範囲内に調整し、加水分解により残存しているニトリル基量の1.0~5.0meq/gにカルボキシル基を、残部にアミド基を導入し、次いで該カルボキシル基の50~90mol%をMg, Ca, Cu, Zn, Al, Ag, Feより選ばれる1種あるいは2種以上の金属塩型とし、最終熱処理の乾熱温度を100~230℃で行なうことにより達成することができる。さらに本発明は上記吸湿性架橋アクリル系繊維を10wt%以上含有してなる繊維構造体である。

【0008】以下、本発明を詳述する。本発明の吸湿速度定数は丹羽、野坂〔織消誌 5, 73 (1964)〕らによって提唱された下記速度式〔I〕により求められる。

$$[I] W = W_0 (1 - e^{-kt})$$

$W$  : 時間 $t$ における吸湿量

$W_0$  : 平衡吸湿量

$k$  : 吸湿速度定数

同報文によると、吸湿速度定数 $k$ は吸湿性の低い合成繊維ほど大きく、アクリルで0.153mm<sup>-1</sup>、ポリエステルで0.173mm<sup>-1</sup>の値を示す。一方、レーヨンは0.032mm<sup>-1</sup>、アセテートは0.078mm<sup>-1</sup>を示す。吸湿性天然繊維の木綿は0.043mm<sup>-1</sup>、羊毛は0.040mm<sup>-1</sup>であり、本発明者が式〔I〕に従って求めた吸湿速度定数は、アクリル0.12mm<sup>-1</sup>、ポリエステル0.13mm<sup>-1</sup>、木綿0.06mm<sup>-1</sup>、羊毛0.04mm<sup>-1</sup>ではほぼ一致する。本発明者は繊維の飽和吸湿率とその吸湿・放湿速度が衣服内あるいは寝具内の調湿・調湿性と関係があり、着心地性や皮膚表面の保温性と密接な関係があることを見出した。即ち、20℃65%RHにおける飽和吸湿率が15~35重量%の範囲内にある高吸湿性繊維であって、且つ吸湿放湿速度定数が木綿以下の特定の範囲に制御することで、環境の温湿度変化に対して、調湿性

に優れた快適な衣服内環境、寝具内環境を維持し得る。

【0009】本発明では、20℃65%RHに於ける飽和吸湿率が15~35重量%であって、上記速度式の吸湿速度定数 $k_1$ が0.015~0.029の範囲で且つ放湿速度定数 $k_2$ が0.005~0.015の範囲であることによって、目的の調湿・調湿機能を達成することができる。20℃65%RHにおける飽和吸湿率を15~35重量%に制御する方法としては、カルボキシル基量の50~90mol%、好ましくは、60~85mol%をMg, Ca, Cu, Zn, Al, Ag, Feより選ばれる1種あるいは2種以上の金属塩型とする方法が採用できる。この範囲を外れる場合には、目的とする吸湿率レベルが得られない。一方、この方法によって得られる繊維は、ほぼ天然繊維の吸湿速度定数を有するが、本発明者らが目的とする吸湿速度定数が0.015~0.029の範囲、放湿速度定数が0.005~0.015の範囲に制御するためには、最終処理の乾熱温度を100~230℃、好ましくは110~210℃で行なうことにより達成される。最終処理温度が下限を下回る場合は、繊維表面の緻密化構造が形成されておらず、吸放湿速度定数は大きくなる。また上限を上回る場合は、繊維の着色や強度低下面から好ましくない。

【0010】本発明は、架橋アクリル系繊維を主とするものであり、アクリル系繊維をヒドラジン処理により架橋結合を導入して、窒素含有量の増加を1.0~8.0重量%、好ましくは3.0~8.0重量%の範囲内に調整し、加水分解処理により、残存しているニトリル基量の1.0~5.0meq/g、好ましくは2.5~5.0meq/gにカルボキシル基を、残部にアミド基を導入し、次いで該カルボキシル基の50~90mol%、好ましくは60~85mol%をMg, Ca, Cu, Zn, Al, Ag, Feより選ばれる1種あるいは2種以上の金属塩型としたものである。したがって、このようにニトリル基が大きく変化したものになっているので、本発明の繊維は架橋アクリル変性繊維と称することもできるのである。該繊維の窒素含有量の増加が下限を下回る場合には、抗ビル性が付与されるが紡績、編織などの加工性を満足し得る物性の繊維が得られず、上限を越える場合には、目的とする吸湿率及び保水性、水吸上げ性、制電性が得られない。上記において、金属塩はMg, Ca, Cu, Zn, Al, Ag, Feより選ばれるが、本発明の調湿・調湿・調和機能を損なわない範囲でこれら以外の金属も使用することができる。しかし、その含有量はカルボキシル基量として、5mol%以下である。

【0011】また、加水分解反応により、ヒドラジン架橋されずに残存しているニトリル基を実質的に消失させ、1.0~5.0meq/gのカルボキシル基部にアミド基を導入する方法としては、アルカリ金属水酸化物、アンモニア等の塩基性水溶液、或いは硝酸、硫酸、

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塩酸等の鉱酸の水溶液を含浸、又は該水溶液中に原料繊維を浸漬した状態で加熱処理する手段が挙げられる。尚、前記架橋結合の導入と同時に加水分解反応を行うこともできる。カルボキシル基が上記下限に満たない場合には吸湿率が低くなり、又上限を越えると吸湿率が高くなり過ぎるために衣服内気候、特に皮膚表面への保湿性を調節できない。また抗ビル性は付与できるが、紡績性、編織などの加工性を得る繊維物性も得られない。

【0012】カルボキシル基を塩型にする方法としては、上述した加水分解繊維を下記に例示する各種の塩型の水酸化物、又は塩の水溶液に浸漬し、しかる後水洗、乾燥する方法が好適に用いられる。ここでカルボキシル基の塩型としては、50～90mol%をMg, Ca, Cu, Zn, Al, Ag, Feより選ばれる1種或いは2種以上の金属と塩型であることが必要である。この範囲を下回る場合には、アルカリ側のpH緩衝性が不足し、架橋構造が不十分のためアンモニアに対する消臭性が不足し、目的とする調和機能が付与できない。一方、この範囲を上回る場合には、酸側のpH緩衝性が不足し、乾燥速度が遅くなりイージーケア性が低下し、目的とする調和機能が付与できない。

【0013】このようにして、20℃65%RH下の飽和吸湿率、及びpH緩衝性、難燃性、抗菌性、消臭性、抗ビル性、制電性、保水性、水吸上げ性、乾燥のし易さなどの調和機能を合わせ有する、健康・快適・安全・衛生及びイージーケア性を備えたアクリル系繊維及びその繊維製品を提供できるのである。更に引張強度を向上させる必要が求められる場合には、後述するように出発アクリル系繊維として二色性比の高い繊維を選ぶのが良い。

【0014】上記吸湿性架橋アクリル系繊維を製造するための装置としては、アクリル系繊維をポンプ循環系を備えた容器内に充填し、上記架橋結合の導入、加水分解反応、及び金属塩の形成の各反応を逐次行う手段が、安全性、均一反応性等の諸点から望ましい。かかる装置（ポンプ循環系を備えた容器）の代表例としては、加圧型オーバーマイヤー染色機等が挙げられる。

【0015】また、目的とする吸湿率と調湿・調湿性機能、ならびにpH緩衝性、難燃性、抗菌性、消臭性、抗ビル性、制電性、保水性、吸水性、乾燥のし易さなどの調和機能を合わせ有し、しかも紡績、編織加工に必要な物性を提供するためには、特に下記特性を備えた出発アクリル系繊維を採用することが望ましい。

【0016】即ち、繊維を形成するAN系重合体分子が十分に配向しておりコンゴレッド（以下CRという）二色性比が0.4以上、更に好ましくは0.5以上のアクリル系繊維を採択することが望ましい。なお、CR二色性比は、高分子化学23(252)193(1966)記載の方法に従って求められるものである。

【0017】なお、かかるアクリル系繊維の製造手段に

限定はなく、上記CR二色性比が満たされる限り、適宜公知の手段を用いることができるが、中でも全延伸倍率を4倍以上、好ましくは8倍以上とし、且つ工程収縮率を40%以下、好ましくは30%以下とする手段の採用により、工業的に有利に所望のアクリル系繊維を製造することができる。

【0018】更に出発アクリル系繊維として、延伸後熱処理前の繊維（AN系重合体の紡糸原液を常法に従って紡糸し、延伸配向されてはいるが、乾燥緻密化、湿熱緩和処理等の熱処理の施されていない繊維、中でも湿式又は乾/湿式紡糸、延伸後の水膨潤ゲル状繊維：水膨潤度は30～150%）を使用することにより、反応液中への繊維の分散性、繊維中への反応液の浸透性などが改善され、以て架橋結合の導入や加水分解反応が均一かつ速やかに行われるので望ましい。なお、水膨潤度とは乾燥繊維重量基準で表した含有水分量の百分率である。

【0019】本発明の繊維構造体の外観形態としては、糸、ヤーン（ラップヤーンも含む）、フィラメント、織物、編物、不織布、紙状物、シート状物、積層体、綿状体（球状や塊状のものを含む）等があり、さらにはそれらに外被を設けたものもある。該構造体内における本発明の吸湿性アクリル系繊維の含有形態としては、他素材との混合により、実質的に均一に分布したもの、複数の層を有する構造体場合には、いずれかの層（単数でも複数でも良い）に集中して存在せしめたものや、夫々の層に特定比率で分布せしめるもの等がある。

【0020】従って本発明の繊維構造体は、上記に例示した外観形態及び含有形態の組合せとして、無数のものが存在する。いかなる構造体とするかは、本発明の繊維が既述の如く多くの機能を有するので、最終製品の使用態様（例えばシーズン性、運動性や內衣か中衣か外衣か、カーテンやカーペット、寝具やクッション、インソールや空調器等としての利用の仕方など）、要求される機能、かかる機能を発現することへの本発明繊維の寄与の仕方等を勘案して適宜決定される。

【0021】さらに構造体を細かく見れば、本発明の吸湿性アクリル系繊維単独で又は他の素材とほぼ均一に混合した状態のものだけでなく、これに他の素材を貼付、接着、融着、挟み付け等で積層あるいはラミネートなど行い、2～5の複数層の積層状となるものがある。また積層状ではあるが、積極的な接合は行わず支持体で積層状を維持するものもある。

【0022】本発明の繊維構造体を利用した最終製品の用途としては、先にも触れたように、大別すると人が着用して利用するもの、布団や枕、クッションの様な寝具類、カーテン、カーペットに代表されるインテリア、調湿や消臭等のその他の分野が挙げられる。そしてこれらの用途に応じ、要求される機能を満たすべく単一層から複数層まで、さらにそれを含んで外被を施すなど、最適な構造を選択するのである。

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【0023】本発明の繊維構造体は前記した通り、本発明の吸湿性アクリル系繊維を10wt%以上含有してなるものである。したがって他の素材例えば繊維、ラバー、ゴム、樹脂、プラスチック等は、全体の90wt%以下の割合で併用されるが、該構造体は本発明の吸湿性アクリル系繊維単独、即ち100wt%でなる場合は、他の素材の併用はない。通常他の繊維との混紡によって構造体とする場合、本発明の吸湿性アクリル系繊維の使用量は10wt%以上100wt%未満、好ましくは10wt%～50wt%である。10wt%未満では本発明の吸湿性アクリル系繊維といえども、十分なレベルの機能が発現できない。本発明の吸湿性アクリル系繊維の含有率は用途によって異なるが、肌着等では10～80wt%、好ましくは10～70wt%、おむつ等では少なくとも10wt%、好ましくは20wt%以上である。使用形態は肌着では他の繊維と混紡して紡績糸として綿織地の形の繊維構造体として用いるのが好ましい。おむつや生理用品等の吸収体や、スポーツ衣料等では、本発明の吸湿性アクリル系繊維単独又は他の繊維と混用してウェットシートとなし、該シートを他の繊維シート又は織物と積層して用いる。本発明の吸湿性アクリル系繊維の特徴を生かすには、肌に接する側に本発明のシートを配設した構造体とすることが好ましい。

【0024】このように他の素材を併用するのは、構造体の機能をさらに高めるのに有用だからである。即ち本発明の吸湿性アクリル系繊維は前述の通り多くの機能を備えるものではあるが、他の素材を併用した構造体とすることにより、さらに高機能を付与する、好ましい風合いを与える、鮮明な染色性などいわゆるファッション性を高める等ができるのである。また、混紡等の加工性を改善する効果も期待できる。

【0025】本発明の繊維構造体において併用しうる他繊維としては特に限定されず、公称されている天然繊維、有機繊維、半合成繊維、合成繊維が用いられ、さらには無機繊維、ガラス繊維等も用途によっては採用し得る。また併用し得る素材は繊維に限らず、前述したようにフィルムとラミネートする、あるいはフィルムに埋設して構造体とするなど、プラスチック、ゴム等も採用し得る。特に好ましい他の繊維を例示すれば、羊毛やコットン等の天然繊維、ポリエステル、ポリアミド、ポリアクリル繊維等の合成繊維あるいはレーヨン、ポリノジック繊維等である。

よく採用する構造体の1つである不織布として、本発明の吸湿性架橋アクリル系繊維を使用する場合は短繊維として、セルロース系繊維、パルプ、合成繊維等と適宜混用して使用することができる。特に寸法安定性が求められる用途においては、本発明の繊維と熱接着性繊維（好ましくは10～80wt%の混用率）とからなる不織布が推奨される。なお熱接着性繊維としては、熱接着性を備えている限り使用でき、例えば、ポリエチレンーポリ

プロピレン、ポリエチレンーポリエステル、ポリエステルーポリエステル等の低融点・高融点成分からなる繊維が挙げられる。本発明の繊維を用いた不織布は、人体に接触して肌に優しく、かつ吸水性を発揮させる用途に好適である。例えばおむつの用途に有用であり、おむつの不織布のトップシートのみならず、バックシートさらにはオムツカバーにも使用でき、高吸水性ポリマーの使用量を減らすこともできる。本発明の繊維は、高吸水性でかつ抗菌性をも有しているため、該繊維を用いたかかる構造体は、長時間着用しても、むれない、かぶれない等の利点を有する。

【0026】

【作用】本発明に係る吸湿性アクリル系繊維が調湿、調湿性能並びに各種調湿機能を合わせ備える理由は、概ね次のように考えられる。

【0027】即ち、本発明に係る繊維は、AN系重合体から出発しているが、実質的にニトリル基が消失しているところから、ポリマー鎖に結合している側鎖は、ヒドラジンとの反応により生成した窒素を含有する架橋構造とニトリル基の加水分解反応により生成した塩型カルボキシル基と考えられる。

【0028】一般に塩型カルボキシル基の塩基は吸湿性を有しており、吸湿することによって水素結合や溶解熱、ファンデルワース力に關与した発熱（吸着熱）を有することが知られている。ここで1価の塩と2価以上の金属塩、及び塩型でないカルボン酸のバランスによって、目的とする吸湿率が設計され、且つ水分の吸着、脱着曲線が一般の吸湿性繊維、例えば木綿、羊毛、レーヨンに比べてヒステリシスが大きくなると推定される（図6参照）。一方、最終熱処理の乾熱温度を高め、繊維表面の緻密性を上げることによって、先のヒステリシスと相乗効果を生み初期の吸湿速度定数を低く制御しているものと推定される。これらが調湿・調湿性能をもたらしているものと考えられる。

【0029】金属塩型とH型との特定比率のカルボキシル基が弱酸性に緩衝性を示すのは、弱塩基の金属塩と弱酸が適度に共存するためである。また難燃性は架橋構造とアクリルアミド及び金属塩により、また抗菌性は架橋構造によりもたらされているものと推定する。制電性は吸湿した繊維内の水分が発生静電気を漏洩させる効果をもたらす、抗ビル性は低強度により、更に高吸湿性は架橋構造と塩型カルボキシル基によるものであろう。又低強度にかかわらず紡績、編織加工性能を支えているのは、CR二色性比にみられる配向構造と多価金属による分子内、分子間のイオン架橋に由来するところが大であらう。

【0030】

【実施例】以下本発明を実施例により具体的に説明するが、本発明はこれらに限定されるものではない。実施例中の部及び百分率は断りのない限り重量基準で示す。

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【0031】なお、pH緩衝能力( $\mu\text{eq/g}$ )、全カルボキシル基量、金属塩型カルボキシル基量、H型カルボキシル基量( $\text{meq/g}$ )、LOI(限界酸素指数)、吸湿率、抗菌性(増減値差)、抗ビル性(ICI等級)、制電性(半減期)、吸水性(吸上げ長)、乾燥時間、保水率、消臭性、吸湿速度定数、放湿速度定数、及び蓄熱量は以下の方法により求めた。

【0032】(1) pH緩衝能力( $\mu\text{eq/g}$ )

$$\text{pH緩衝能力}(\mu\text{eq/g}) = \frac{1000Y}{X}$$

【0033】(2) 全カルボキシル基量( $\text{meq/g}$ )

十分乾燥した供試繊維約1gを精秤し(X)g、これに200mlの1N塩酸水溶液を加え30分間放置したのちガラスフィルターで濾過し水を加えて水洗する。この塩酸処理を3回繰り返したのち、濾液のpHが5以上に

$$\text{全カルボキシル基量}(\text{meq/g}) = \frac{X}{0.1Y}$$

【0034】(3) 金属塩型カルボキシル基量( $\text{meq/g}$ )

十分乾燥した供試繊維を精秤し、常法に従って濃硫酸と濃硝酸の混合溶液で酸分解したのち、金属を常法に従って原子吸光度法により定量し、金属の結合したカルボキシル基量として算出し、全カルボキシル基に対するモル分率で表した。

【0035】(4) H型カルボキシル基量( $\text{meq/g}$ )

次式によりH型カルボキシル基量を算出した。H型カルボキシル基量=全カルボキシル基量-金属塩型カルボキシル基量

【0036】(5) LOI

JIS-7201の最低酸素指数の測定法に従って行った。

【0037】(6) 吸湿率(%)

試料繊維約5.0gを熱風乾燥機で105℃、16時間乾燥して重量(W1)gを測定する。次に試料を温度20℃で相対湿度65%に調整された恒温恒湿機に24時間入れて置く。このようにして吸湿した試料の重量(W2)gを測定する。以上の結果から、吸湿率を次式に従って算出した。

$$\text{吸湿率}(\%) = \frac{W2 - W1}{W1} \times 100$$

【0038】(7) 抗菌性

試験菌株：黄色葡萄球菌 *Staphylococcus aureus* IF 0 12732

試験方法：繊維製品衛生加工協会(SEK)で定める方法により、滅菌試料布に試験菌のブイオン懸濁液を注

十分乾燥した供試繊維約0.4gを精秤し(X)g、これに200mlの水を加えた後、0.1N塩酸水溶液あるいは0.1N苛性ソーダ水溶液を滴下し、塩酸水溶液の場合はpH5.0になるまでに、また苛性ソーダ水溶液の場合はpH7.0になるまでに消費された塩酸水溶液または苛性ソーダ水溶液消費量(Y)ccを求め、次式によって、酸またはアルカリに対する緩衝能力を算出した。

$$1000Y$$

X

なるまで十分に水洗する。次にこの試料を200mlの水に入れ1N塩酸水溶液を添加してpH2にした後、0.1N-苛性ソーダ水溶液で常法に従って滴定曲線を求めた。該滴定曲線からカルボキシル基に消費された苛性ソーダ水溶液消費量(Y)ccを求め、次式によって全カルボキシル基量を算出した。

$$0.1Y$$

X

加し、密閉容器中で、37℃、18時間培養後の生菌数を計測し、植菌数Aに対する標準布の菌数Bと試料の菌数Cの増減値差で求める。

$$\text{増減値} = \log C - \log A$$

$$\text{増減値差} = (\log B - \log A) - (\log C - \log A)$$

【0039】(8) 抗ビル性

JIS L 1076繊維及び編物のピリング試験方法A法のICI型試験機を用いる方法に従って行った。

【0040】(9) 制電性

JIS L 1094繊維及び編物の帯電性試験方法に従って行なった。

【0041】(10) 吸水性

JIS L 1018メリヤス生地試験方法、吸水速度B法(バイレック法)に基づき、測定開始30分経過後の吸上げ長(cm)を求めた。

【0042】(11) 乾燥時間

試料編地10×10cmを純粋中に1時間浸漬後、遠心脱水機(KUBOTA(株)製)を用いて300Gの回転で2分間の脱水処理を行う。このようにして含水した試料を雰囲気20℃65%RH内に設置したテンシロン/UTM-II-20型に取付け、試料の重量変化と時間を測定し、触感における乾燥時間を求めた。

【0043】(12) 保水率(%)

試料繊維5gを純水中に浸漬し、30±5℃で3時間放置後、遠心脱水機(KUBOTA(株)製)を用いて1000Gの回転で3分間脱水処理を行う。このようにして脱水した試料の重量(W3)gを測定する。次に該試料を90℃の熱風乾燥機内で、絶乾まで乾燥した試料の重量(W4)gを求め、次式によって保水率(%)を算



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出した。

$$\text{保水率 (\%)} = \frac{W3 - W4}{W4} \times 100$$

【0044】(13) アンモニア消臭性  
試料繊維2gをテドラーバッグに入れ密封し、空気を3l注入する。次に400ppmのアンモニア(W5)をテドラーバッグ内に注入し、室温で120分放置後にテ

$$\text{アンモニア消臭率 (\%)} = \frac{W5 - W6}{W7} \times 100$$

【0045】(14) 吸湿速度定数 ( $k_1$ )  
5×20cmの編地を105℃熱風乾燥機で絶乾後、デシケーター内で20℃に冷却する。20℃65%RHに調整した恒温恒湿器(タバイ製 タイプLHL-112T)内に編地を置き、120分間経過時間に対する吸湿率( $W_1$ )を連続的に測定する。該編地を更に24時間恒温恒湿器に入れて置き、飽和吸湿率( $W_s$ )を測定する。下記速度式の吸湿速度定数( $k_1$ )を算出する。

$$W_1 = W_s \cdot (1 - e^{-k_1 t})$$

$W_1$  : 絶乾から時間tにおける吸湿率

$W_s$  : 20℃65%RH飽和吸湿率

$k_1$  : 吸湿速度定数

t : 0~30分

【0046】(15) 放湿速度定数 ( $k_2$ )  
5×20cmの編地を20℃80%RHに調整した恒温恒湿器に24時間入れておき、同温湿度における飽和吸湿率( $W_b$ )を測定する。該編地を20℃30%RHに調整した恒温恒湿器内に置き、120分間経過時間に対する吸湿率( $W_2$ )を測定する。更に編地を20℃30%RH恒温恒湿器内に24時間入れておき20℃30%RHにおける飽和吸湿率( $W_a$ )を測定する。下記速度式の放湿速度定数( $k_2$ )を算出する。

$$W_2 = (W_a - W_b) \cdot (1 - e^{-k_2 t})$$

$W_2$  :  $W_b$  から時間tにおける吸湿率

$W_a$  : 20℃30%RH飽和吸湿率

$W_b$  : 20℃80%RH飽和吸湿率

$k_2$  : 放湿速度定数

t : 0~30分

【0047】(16) 蓄熱量 (℃・Hr)

カード掛けし絶乾した試料繊維2.5gを直径4.5cm、長さ6.0cm、のポリエステル布帛の袋に充填し、中央に温度検出端を挿入する。該試料を20℃90%RHに調整した恒温恒湿器内に吊し、布帛内温度を連続的に自記記録する。0~1時間雰囲気温度に対する増加温度を積分し、蓄熱量(℃・Hr)と定義した。

【0048】実施例 1

アクリロニトリル90%及びアクリル酸メチル10%のアクリロニトリル系重合体を48%のロダンソーダ水溶液で溶解した紡糸原液を常法に従って紡糸、水洗、延

ドラッグバッグ内のアンモニア濃度(W6)を北川式検知管を用いて測定した。また、試料を入れないテドラーバッグに400ppmのアンモニアを注入し、120分後にアンモニア濃度(W7)を測定し空試験とした。以上の結果から、次式に従って、アンモニア消臭率を算出した。

$$\text{アンモニア消臭率 (\%)} = \frac{W5 - W6}{W7} \times 100$$

伸、捲縮、熱処理をして、0.8デニール×70mmの原料繊維を得た。この原料繊維1kgに30重量%の加水ヒドラジン5kgを加え、98℃で3時間架橋処理した。窒素増加量は5.0%であった。該架橋繊維を水洗後、更に3重量%の水酸化ナトリウム5kgを加え、90℃で2時間加水分解した。次いで、1規定HNO<sub>3</sub>水溶液で処理して、カルボキシル基をH型に変換し、水洗後、1規定NaOHでpHを6.5に調整し、塩化カルシウム50gを添加して、60℃で2時間金属塩処理した。十分水洗した後、脱水、油剤処理及び表1に示す熱処理を行い、架橋アクリル系繊維を得た。繊維のカルボキシル基は、4.3meq/g、全カルボキシル基中のCa型カルボキシル基は80mol%であった。

【0049】得られた繊維の特性を表1に示す。本発明例の繊維No. 1~3の吸湿率は、25~28%であり、木綿の約3.5倍と高い。また20℃65%RH雰囲気下での吸湿速度曲線を図1に放湿速度曲線を図2に示した。これらの曲線から得た初期の0~30分での吸湿速度定数 $k_1$ 及び放湿速度定数 $k_2$ を表1に示したが、 $k_1$ 、 $k_2$ は最終熱処理温度を高めることで低下せしめる傾向が明瞭に示されている。一方、20℃65%RH下での繊維内温度の吸着発熱・放熱曲線を図3に示す。図3で明らかな如く吸湿に伴う吸熱でいずれの繊維も発熱するが、 $k_1$ の大きい繊維ほど吸着発熱反応が速く完了するため、雰囲気温度までの冷却時間が短い。対して、本発明例の繊維は、 $k_1$ が小さい効果で吸着発熱が持続するため、放熱に伴う冷却速度が遅く、60分経過後の繊維内温度は、木綿に対して約+4℃、羊毛に対して約+3℃高く、且つ保温性の尺度となる0~60分間の蓄熱量は木綿の2倍以上、羊毛の1.5倍以上である。これらの結果から飽和吸湿率と $k_1$ が発熱量と蓄熱量に大きな影響を与えることが証明される。また本発明例の繊維の保水率は、木綿レベルの高い値を示す。一方、難燃性の尺度であるLOI値は、29~30と高く、マッチで着火しても全く燃焼しない。更にアンモニア消臭率も95%以上と高く、アンモニアに対して高度の消臭機能を有することが判明した。

【0050】

【表1】

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表 1

例	繊維 No.	熟処理 温度 (°C)	吸湿率 (%)	蓄熱量 (°C Hr)	吸湿速度 定数 $k_1$ (mm <sup>-1</sup> )	放湿速度 定数 $k_2$ (mm <sup>-1</sup> )	pH緩衝性 ( $\mu\text{eq/g}$ ) 酸 アルカリ	保水率 (%)	難燃性 LOI	アプレ 消臭率 (%)
本発明例	1	120	28	6.1	0.020	0.010	1300 350	47	30	98
本発明例	2	200	25	6.0	0.015	0.003	1200 400	47	29	95
本発明例	3	150	27	6.5	0.018	0.007	1400 350	47	29	99
比較例	木綿	—	7	2.6	0.035	0.060	200 0	45	17	—
比較例	羊毛	—	12	3.9	0.065	0.020	250 0	35	23	—
比較例	アクリル	—	1.5	0.3	0.117	0.090	250 0	15	18	17
比較例	ポリエステル	—	0.3	0.2	0.132	0.042	200 0	10	21	—

木綿：コーマ

アクリル：アクリル繊維エクスラン K8-1.5<sup>φ</sup> 51mm

## 【0051】実施例 2

実施例1で作成した本発明例の繊維No. 3 (1.8<sup>d</sup> × 4.8<sup>mm</sup>) をアクリル繊維 (エクスラン; 1.5<sup>d</sup> × 5.1<sup>mm</sup>) 及びコーマ綿と混紡率を変化して常法に従って、混紡、カード、練糸、粗紡を行い、1/52メートル番手、撚数830T/Mの糸を作成した。比較例としてアクリル繊維、カットウール、コーマ綿、及びポリエステル繊維 (東洋紡; 1.5<sup>d</sup> × 5.1<sup>mm</sup>) について同様に、糸を作成した。次にこれらの糸を20ゲージのスムーズ編機で目付が200±20 g/m<sup>2</sup> の編地を作成した。次いで、この編地を回転バッグ染色機で精練を行い、乾燥後ホフマンセット機で編地サンプルA～Fを作成した。編地サンプルA～Fの詳細と特性値を表2に示す。本発明例の繊維を100%使った編地A-1は表1で測定した原綿繊維と同レベルの抗菌性と消臭性、LOI値、吸湿率、pH緩衝性を再現した。抗ビル性は、5級であり毛玉は全く発生しなかった。制電性は、半減期1秒と木綿レベルを示した。また、水吸上げ長は、木綿の約1.2倍である。更に、保水率は木綿と同レベルで、且つ吸湿率が木綿の約3.5倍と大きいにもかかわらず、

感触における乾燥時間は木綿の3倍以上速く、親水性でしかも乾きが速く湿潤感が少ないというイメージがあることが判明した。一方、本発明例の繊維とアクリル繊維又は木綿とを混紡したものにおいては、混紡率に対してLOI値の低下が大きく難燃効果は小さいが、他の抗菌性、消臭性、抗ビル性、制電性、pH緩衝性や乾燥速度は混紡率換算値と同等以上の性能が得られ、特筆すべき効果として水吸上げ速度はアクリル繊維が混紡された方が素早く吸水するという相乗効果を見出した。これは、アクリル繊維のみならずポリエステル繊維など疎水性繊維が混紡されるほど毛細管速度が促進され、混紡効果が大きい可能性を示唆している。このように本発明の繊維は、肌着、セーター、ランジェリー、ブラジャー、スウェットスーツ、スポーツウェア、トレーナー、レオタード、手袋、靴下、サポーター類、タイツ、パジャマ等で代表される衣料用編地においても多機能を有する画期的な商品を提供し得るものであることが証明された。

【0052】

【表2】



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表 2

編 地 サンプル	使用繊維 (%)	抗菌性 菌数増 減値差	難燃性 LOI	アンモニア 浸透率 (%)	抗ビル 性ICI (級)	制 電 性 半 減 期 (秒)	吸湿率 (%)	pH緩衝性 (μeq/g/%) 酸   7.477		水吸上げ長 (mm)	乾 燥 時 間 (分)
本発明例 A-1	本発明例 No. 3 = 100	5.4	28	99	5	1	27	1600	320	145	70
本発明例 A-2	本発明例 No. 3 / アクリル = 50 / 50	5.0	22	99	4	5	15	1550	320	170	55
本発明例 A-3	本発明例 No. 3 / アクリル = 30 / 70	4.7	20	98	3	14	8	1520	300	25	50
本発明例 B	本発明例 No. 3 / 木綿 = 30 / 70	3.5	19	97	5	1	16	1200	240	150	120
比較例C	木 綿 = 100	0.4	17	-	4	1	7	200	0	120	240
比較例D	羊 毛 = 100	0.3	23	-	2	60	16	250	5	5	70
比較例E	ア ク リ ル = 100	1.0	18	12	1	120<	2	250	0	100	40
比較例F	ポリエステル = 100	0.9	21	-	1	120<	0.3	200	0	1	40

木 綿: コーマ

アクリル: アクリル繊維エクステン K8-1.5<sup>°</sup> 51mm

## 【0053】実施例 3

実施例2で作成した編地の調湿・調湿効果をより実際に確認するため、本発明例の編地A-1及び比較例の編地としてCの木綿、Eのアクリルの3点について、縦10cm×横10cmの編地を2つ折りにし、その中央部に温湿度センサー（THP-23 神栄（株）製）を挿入して、データーストッカー（TRH-DM3 神栄（株）製）と接続し、恒温恒湿器（タイプLHL-1122T 田葉井製作所製）内で、20℃80%RHと20℃30%RHの温湿度で各々60分間隔で連続的に変化して、その時の編地内部の温湿度を記録した。湿度変化を図4に、温度変化を図5に示す。吸湿率が低く吸湿・放湿速度定数 $k_1$ ・ $k_2$ が大きいアクリル編地は環境変化にほぼ連動して、湿度が変化し何ら調湿機能を示さない。一方、吸湿性天然繊維である木綿は繊維自体の吸湿放湿機能により、繊維内温度は環境変化に対してある程度遅れる傾向を示す。これに対して本発明例の繊維編地は吸湿率が高く、吸湿・放湿速度定数 $k_1$ ・ $k_2$ が低い特性を有することから、環境変化に対して繊維内温度の変化が少なく約50%RHから約70%RHの快適湿度に調湿されていることが確認された。また繊維内温度については、アクリル編地は环境温度20℃に対してはほぼ変化を示さないのに対し、木綿編地は高温時には2～3℃の吸湿発熱の昇温を示す反面、高温から低温下に変化した場合には放湿によって気化熱が奪われ、环境温度20℃以下まで下がり着用時に冷え感を生じる事象と一致する。これに対して、本発明例の繊維は吸湿能力が高く、且つ吸湿・放湿速度定数 $k_1$ ・ $k_2$ が小さい効果で、吸湿発熱温度が高く、且つその温度保持時間が長く、保温性とその調湿性に優れた特徴を有することが確認された。

## 【0054】実施例 4

実施例2で作成した本発明例繊維No. 3. 30%・ア

クリル70%の混紡糸A-3、及びアクリル100%糸Eの1/36メートル番手糸を用いて1.65±0.05kg/枚、目付パイル長6mmの両面起毛ニューマイヤー毛布を各5枚づつ試作した。この毛布各々1枚を破壊試験に供し、残り各4枚を4名の着用試験者に配付して、アンケート方式による実用試験を行なった。各試験結果を表3及び表4に示す。尚、実用試験は1月中旬～2月下旬の冬期に実施し、掛け布団、敷き布団は規制しなかった。表3に示す防炎性は、防炎製品性能試験基準である45°メセナミン法、及び45°タバコ法でJIS L 0217の103法に基づいた洗濯処理5回後に測定した。本発明のA-3の編地を使用した毛布では、実施例3の編地で測定しなかった摩擦帯電率は3.0kVであり、半減期は編地より低い値を示し、実用制電効果を確認した。一方、編地のLOIでは効果の少なかった難燃性の混紡効果は、A-3の編地を使用した毛布の防炎性に対しては、45°メセナミン法、45°タバコ法共に合格した。これは編地のような垂直法より条件が甘いこと、及び本繊維が通常の合成繊維のように熔融延焼する挙動を示さず、炭化し易いことによる防炎効果と推定される。また、抗菌性、消臭性は実施例3の編地とほぼ同等の効果を示した。また表4には、4名の着用試験者のほぼ共通したアンケート結果を示したが、本発明のA-3の編地を使用した毛布は、通常冬物に使用されるアクリル100%毛布に比べて、速暖性が有ることが確認された。人が布団に入って、寝つくまでの時間は約1時間以内であり、速暖性は安眠を促す効果として期待できる。また、その他の感想では早朝の足元の冷え感がないことが挙げられたが、これは足先は発汗量が多いため、吸湿率が低く且つ吸放湿速度が速いアクリル繊維は水分蒸発による気化熱で冷え感が出ることが予測され、本発明の繊維の他の特徴として注目される。一方、本発明繊維の毛布が爽やかな感じがするという感想については、

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実施例3の編地による温度変化に対する調湿効果と因果関係があると推定され、春夏用毛布での着用試験も非常に興味のあるところである。なお、参考のため、図7(a)、図7(b)に毛布A-3の毛布内の温度・湿度経時変化の測定結果を示す。このように本発明の繊維は

表 3

使用編地 No.	使用繊維 (%)	JIS-L-1094		防炎性		抗菌性	消臭性
		摩擦帯電圧 (KV)	半減期 (秒)	45° メセナミン法	45° タバコ法	菌数 増減値差	アンモニア 消費率 (%)
A-3	本発明例No. 3/アクリル =30/70	3.0	1.8	炭化長 43mm 合格	残炭、残炭 なし 合格	3.8	99
E	アクリル=100	5.8	12	炭化長 120mm 不合格	残炭、残炭 あり 不合格	1.2	18

【0056】

表 4

【表4】

使用編地 No.	使用繊維 (%)	着用時の 暖かさ	ムレ感	その他の感想
A-3	本発明例No. 3/アクリル =30/70	即暖性がありEより暖かい	なし	・サンプルE使用時は早期足元部分が冷える感じがするが、サンプルA-3は冷え感が無い。 ・サンプルA-3はサンプルE及びこれまで使用していた毛布に較べてさわやかな感じがする。
E	アクリル=100	暖かい	なし	

【0057】実施例 5

実施例1で作成した本発明例繊維No. 3 (1.8<sup>d</sup> × 48<sup>mm</sup>) 30%とアクリル繊維 (エクスランK8-1.5<sup>d</sup> × 51<sup>mm</sup>) 70%とを均一に混紡した1/52メートル番手 (撚数700T/M) を紡績した。その糸をパッケージ染色機にて染色した後にPVAを主成分とした糊剤を用いて糊付整経した経糸と、パッケージ染色機にて染色し糊付けを行っていない緯糸とを高速織機を用いて経糸密度90本/インチ、緯糸密度70本/インチの平織組織に織り上げ、脱糊精練して風合調整剤 (アニオン系柔軟剤など) を織物に対して0.3重量%付着処理し、乾熱温度150℃の熱風乾燥機で1分間熱処理し、目付120g/m<sup>2</sup> の本発明の繊維構造体である織物サンプルを作成した。

【0058】このようにして作成した織物サンプルの性能を評価した結果、吸湿性、pH緩衝性、抗ビル性、制電性、アンモニア消臭性、抗菌性、吸水乾燥性が表2の

編地サンプルA-3と同程度の能力を有することを見いだした。かかる織物はシャツ地用途において良く適合している。尚、織物の設計を変更することによってスーツ、トランクス、スカーフ、マフラー、ハンカチーフなどの衣料品、シーツ、布団地などの寝装具品に適用し得る。又、他素材との複合 (混紡、交撚、交織などの手法) による繊維構造体も本発明例繊維No. 3を含有することの有用性から示唆される。

【0059】実施例 6

実施例1で作成した本発明例繊維No. 3 (1.8<sup>d</sup> × 48<sup>mm</sup>) を50重量%、ポリエステル熱融着繊維 (2<sup>d</sup> × 51<sup>mm</sup>) を20重量%、アクリル繊維 (エクスランK8-1.5<sup>d</sup> × 51<sup>mm</sup>) を30重量%用い、混綿機で予備開織を行った後、原綿供給ラチス、フラットカード、カードウェッジ重ね装置とニードリング装置が連結した装置で厚さ3mm、目付600g/m<sup>2</sup> のニードルパンチ布帛を作成した。この後、160℃、60秒の熱処理

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を施し引き続いて160℃に設計した2本のカレンダーローラー間を10m/分で通過させて厚さ2.5mmの本発明の繊維構造体である不織布(A)を作成した。

【0060】同様にして、アクリル繊維(エクスランK8-1.5<sup>d</sup>×51<sup>mm</sup>)を80重量%、ポリエステル熱融着繊維(2<sup>d</sup>×51<sup>mm</sup>)を20重量%用いてなる厚さ2.5mmの比較例の不織布(C)を作成した。不織布(A)用の目付1/2量のカードウェーブを上、不織布(C)用の目付1/2量のカードウェーブを下に1対1に重ね合わせた後ニードリング以降を同一条件で通し

2層構造の厚さ2.5mmの本発明の繊維構造体である不織布(B)を作成した。これら(A)、(B)、

(C)の不織布を裁断縫製して靴下敷材を作成した。

【0061】3名の成人男性パネラーを選定し、各人に新品の靴(クラリーノ製)3足ずつと(A)、(B)、(C)各1枚の靴下敷材を支給し、1週間単位で靴及び靴下敷材を交換し3週間ずつの着用試験を実施した。表5にその試験結果を示す。

【0062】

【表5】

表 5

不織布 サンプル	靴下敷材 製品						着用試験結果(3週間着用)		
	重量 g/足	厚み mm	吸湿率% 20℃85%RH	水吸上長 mm	抗菌性 増減値差	アンモニア 消臭率%	蒸れ感	靴下の 濡れ	靴の臭気
本発明(A)	28.2	2.4	22.4	85	3.8	98.5	殆ど 感じない	なし	殆ど 臭わない
本発明(B)	28.0	2.4	22.0	98	5.2	99.8	感じない	なし	殆ど 臭わない
比較例(C)	28.1	2.4	1.6	36	1.0	7.3	蒸れ感 あり	なし	臭いあり

【0063】本発明繊維の繊維構造体である(A)、(B)の靴下敷材は、比較例(C)の靴下敷材に比べて蒸れ感が殆ど感じられず、又、靴下の濡れによる不快感はなく無かった。一方、着用後の靴の臭気も少ない極めて快適な性能を有することが判った。これは、本発明繊維である繊維構造体が、吸湿率、吸水性に優れ、且つ抗菌性に優れる効果によるものであり、靴下敷材用途や敷物用途に良く適合していることを示している。また、本発明の繊維構造体はアンモニア消臭率が極めて高い特長を活かしてオムツカバー、失禁パット、トイレタリー、フィルター類で代表される健康、衛生商品や水、空気浄化商品に応用し得る。又、不織布の製法、混用率、混用相手、複合方法の設計を変化させることによる繊維構造体も本発明繊維No. 3を含有することの有用性から示唆される。

【0064】実施例 7

アクリル繊維100%(エクスランK691-3<sup>d</sup>×70/K89-3<sup>d</sup>×64=60/40のメートル番手2/28')。を総染色機を用い定法にて染色、柔軟処理したもの)パイル糸と、ポリエステル糸(インターレース150<sup>d</sup>/34<sup>f</sup>)を地糸に使用してメリヤスボア編機

で定法に従い編み、その後、毛割り、ポリッシング、毛割り加工でパイル長6mm、目付400g/m<sup>2</sup>のパイル編地を作成した。一方、実施例1で作成した本発明繊維No. 3(1.8<sup>d</sup>×48<sup>mm</sup>)を50重量%、中空ポリエステル繊維(3<sup>d</sup>×51<sup>mm</sup>)を50重量%用い混綿機で予備開繊を行った後、ローラーカードで本発明の繊維構造体であるカードウェーブを作成した。本発明繊維混用ウェーブを詰め綿に使用して、ぬいぐるみを作成した。

【0065】このぬいぐるみを5名の女性パネラーに渡しアンケート方式で着用試験を実施した結果、抱っこしていると温かくなり気持ちが良い、枕かわりに使用すると気持ちが良い、ぬいぐるみがサラッとした感じがするなどの興味ある能力を見いだした。これは、手、或いは肌からの感知汗、不感知汗を通して本発明繊維の備えている吸湿発熱性能が寄与したものと推察され、中綿、詰め綿としての繊維構造体において良く適合していることがわかる。本発明繊維である繊維構造体は、その他にpH緩衝性、抗菌性、アンモニア消臭性などの機能も合わせ備えていることから、布団の中綿、枕の中綿、座布団の中綿、汗取りパット中綿などに応用し得ることが示唆

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される。

## 【0066】実施例 8

本発明繊維No. 3から、実施例6の不織布(A)と同様の方法で、目付100g/m<sup>2</sup>、厚さ3mmのカードウェブシート(A)を、高吸水性繊維(日本エクラン工業(株)製 ランシール)で同じ目付、厚さの高吸水性繊維シート(C)を作製した。さらに吸水性ポリマー(B)ポリアクリル酸の部分架橋物でなると、100%綿でなるガーゼ織物(D)を用意した。これから、上から下にD・A・B・C・Dの順に積層し、本発明構造体であるクロスステッチ積層構造体とした。該吸水性構造体5cm<sup>2</sup>大の上側から0.5wt%アンモニア水溶液を4cc吸収させた後、該構造体を100ccの蒸留水に浸漬し、pHを測定した。pH値は6.5であった。アンモニア吸収後も臭いが無く、またpHがこのように安定しているのは緩衝性に優れることを物語るものである。

## 【0067】

【発明の効果】本発明により、健康・快適・安全・衛生ならびにイージーケア性など多機能を有する調湿・調湿・調和繊維、言い換えれば、コンディショニング機能繊維を提供することができる。本発明の調湿・調湿機能は、20℃65%RHにおける飽和吸湿率が15~35重量%であって、吸放湿速度定数が特定の範囲にあって初めて発揮し得る。また、本発明の繊維はpH緩衝性、難燃性、抗菌性、制電性、消臭性、抗ビル性、保水性、水吸上げ性、乾燥のし易さなど殆どの調和機能を具備しており、従来の天然繊維や合成繊維と比べて顕著な諸機能を有する。更に、各種繊維との混紡の効果も顕著であり、様々な加工や用途分野に広く用いることが可能であ

る。

【0068】すなわち、本発明の繊維を10wt%以上含有する繊維構造体は、併用する相手素材と協同することにより本発明の繊維の少量使用でも十分機能を発現したり、さらに別の機能を併せ有するようにし得るので、多くの最終製品を提供する。

【0069】その一例としては、肌に接する衣料用途として肌着、ランジェリー、パジャマ、乳児製品、ガードル、ブラジャー、靴下、タイツ、レオタード、トランクス等が挙げられ、中外衣料用途としてはセーター、トレーナー、スーツ、スポーツウェア、スカーフ、ハンカチ、マフラー、人工毛皮、乳児製品等が挙げられる。また寝装、建築用途としてはカーペット、マット等の敷物類、毛布、カーテン、布団地、シーツ、中綿、詰め綿等が挙げられ、その他の用途としてはフィルター、吸着材、サポーター、ぬいぐるみ、包帯、止血材、創傷保護用傷当て等が挙げられる。本発明の繊維のpH緩衝性に優れる特徴を生かすためには、肌に接する衣料用途、あるいはオムツ、オムツカバー、生理用品等に用いることが望ましい。

## 【図面の簡単な説明】

【図1】各種繊維の吸湿速度曲線を示したものである。

【図2】各種繊維の放湿速度曲線を示したものである。

【図3】各種繊維の吸着発熱・放熱曲線を示したものである。

【図4】繊維内の湿度経時変化を示したものである。

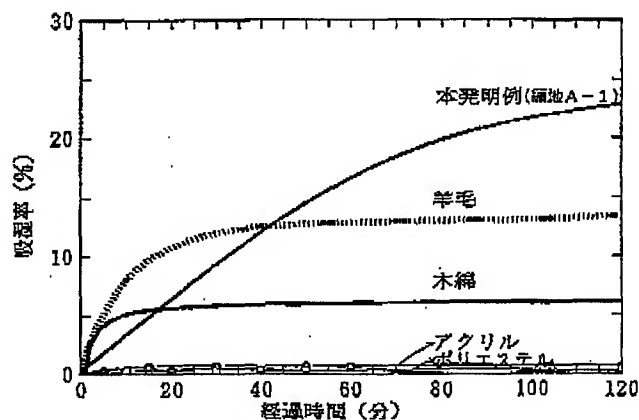
【図5】繊維内の温度経時変化を示したものである。

【図6】繊維の等温吸湿曲線を示したものである。

【図7】(a)は毛布内温度経時変化を、(b)は毛布内湿度経時変化を示したものである。

【図1】

図1 各種繊維の吸湿速度曲線

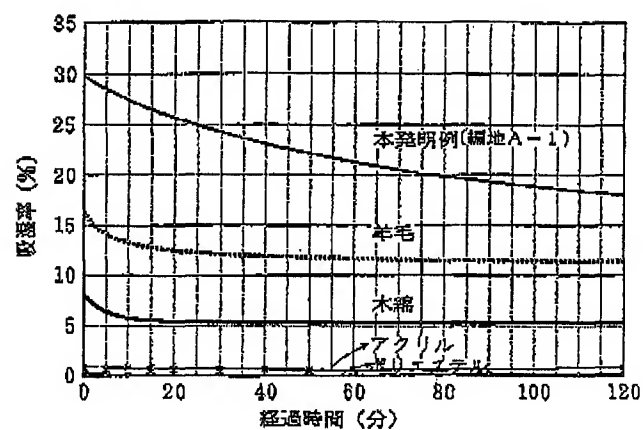


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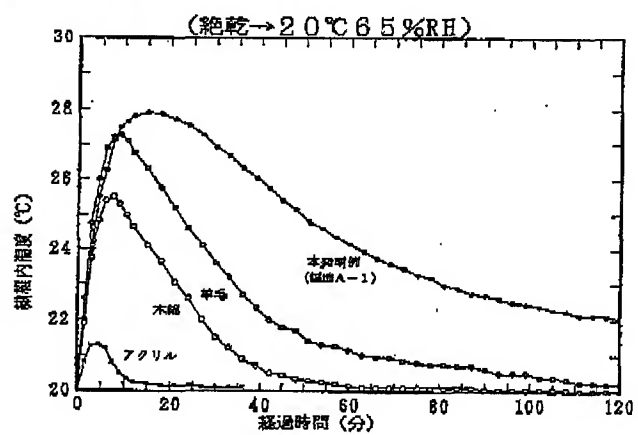
【図2】

図2 各種繊維の放湿速度曲線



【図3】

図3 各種繊維の吸着発熱・放熱曲線

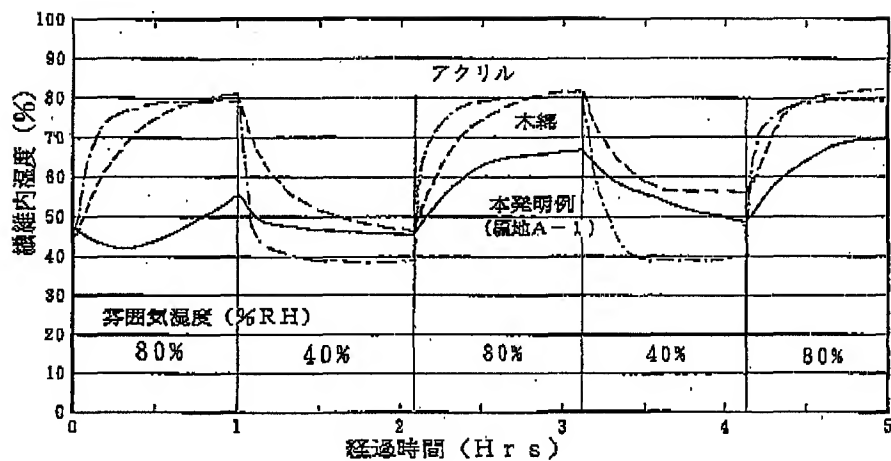


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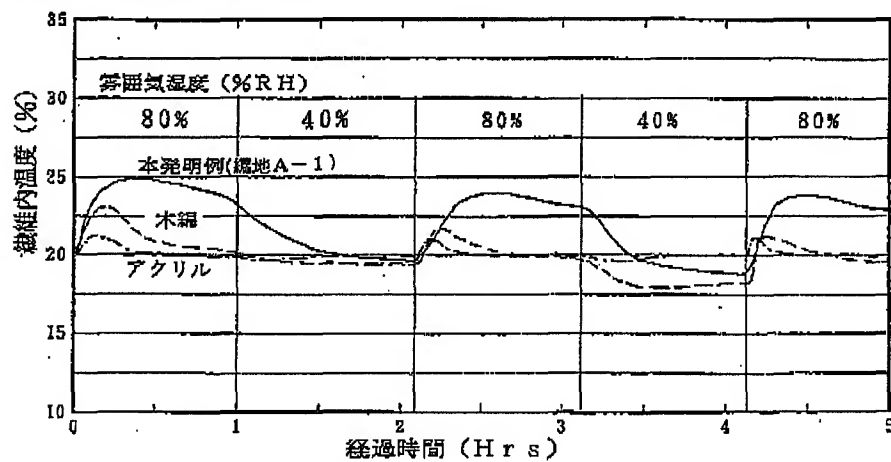
【図4】

図4 繊維内の湿度経時変化



【図5】

図5 繊維内の温度経時変化



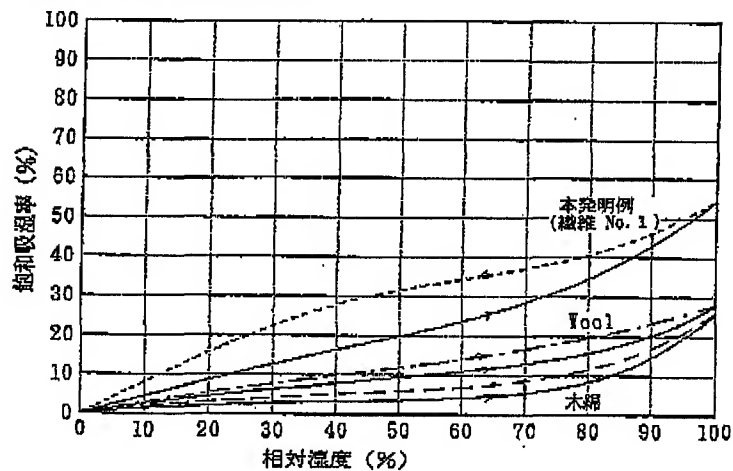


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【図6】

図6 繊維の等温吸湿曲線



【図7】

寝具（毛布）内の温度・湿度経時変化

図7 (a)

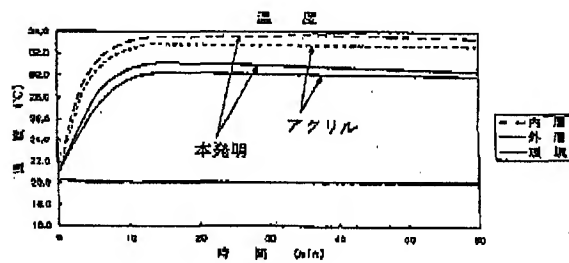
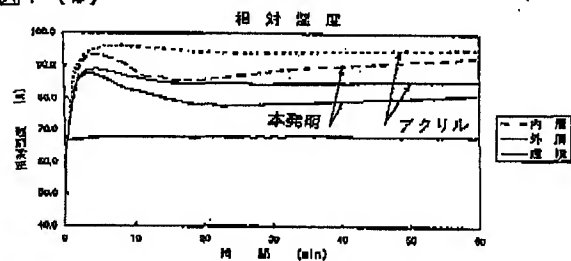


図7 (b)



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技術表示箇所

A

E

L

## HYDROSCOPIC CROSS-LINKABLE ACRYLIC FIBER AND FIBER STRUCTURE USING THE SAME

**Publication number:** JP9059872

**Publication date:** 1997-03-04

**Inventor:** OI YASUHIRO; NAKAJIMA SHIGERU; YASUI HIROMI

**Applicant:** JAPAN EXLAN CO LTD

**Classification:**

- international: **D01F6/18; D01F6/38; D01F6/54; D02G3/04; D03D15/00; D04H1/42; D06M13/02; D06M13/322; D06M13/325; D06M13/338; D06M101/00; D06M101/16; D06M101/18; D06M101/28; D01F6/18; D01F6/28; D01F6/44; D02G3/04; D03D15/00; D04H1/42; D06M13/00; D01F6/44; (IPC1-7): D06M13/338; D01F6/18; D01F6/38; D01F6/54; D02G3/04; D03D15/00; D04H1/42**

- European:

**Application number:** JP19950203846 19950717

**Priority number(s):** JP19950203846 19950717; JP19950162867 19950605

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### Abstract of JP9059872

**PROBLEM TO BE SOLVED:** To obtain a fiber which comprises a temperature-regulating and humidity-controlling highly hygroscopic fiber having controlled moisture absorbing and releasing rate, has regulating functions such as pH adjusting properties, flame retardance, antimicrobial properties, deodorizing properties, pilling resistance, antistatic properties, water retention, water sucking up properties, readily drying, etc., and also health/pleasantness/safety/sanitation/easy care. **SOLUTION:** This hygroscopic cross-linkable acrylic fiber has temperature- regulating and humidity-controlling function of 15-35wt.% saturated moisture absorption at 20 deg.C at 65% RH, 0.015-0.029 coefficient of moisture absorption rate K1 of the formula,  $W1 = We (1 - e^{-k1t})$  [wherein W1 is moisture absorption ratio at time (t) from an absolute dry state; We is saturated moisture absorption ratio at 20 deg.C at 65% RH; K1 is coefficient of moisture absorption rate, and (t) is 0-30 minutes] and 0.005-0.015 coefficient of moisture releasing rate K2 of the formula,  $W2 = (Wa - Wb) (1 - e^{-k2t})$  [W2 is moisture absorption ratio at time (t) from Wb; Wa is saturated absorption ratio at 20 deg.C at 30% RH; Wb is saturated moisture absorption ratio at 20 deg.C at 80% RH; K2 is coefficient of moisture releasing rate, and (t) is 0-30 minutes].

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JP-A-09-059872

[Title of the Invention]

MOISTURE-ABSORBING CROSS-LINKING ACRYLIC FIBER AND A FIBER  
STRUCTURE USING THE FIBER

[Abstract]

[Objects] To provide a temperature-adjusting and moisture-adjusting highly moisture-absorbing fiber where the speeds of absorption and desorption of moisture are controlled in which the fiber has adjusting functions such as pH buffering property, flame retarding property, antibacterial property, deodorizing property, anti-pilling property, antistatic property, water-retaining property, water-sucking property and easily drying property and is equipped with health, comfort, safety, hygiene and easy care properties.

[Constitution] A moisture-absorbing cross-linking acrylic fiber, characterized in that, a saturated hygroscopic rate at 20°C and 65% RH is 15 to 35% by weight, a hygroscopic speed constant  $k_1$  in the following rate equation is within a range of 0.015 to 0.029 and a moisture-desorbing speed constant  $k_2$  thereof is within a range of 0.005 to 0.015.

$$W_1 = W_e (1 - e^{-k_1 t})$$

$W_1$ : moisture-absorbing rate within the time  $t$  from absolute drying

$W_e$ : saturated moisture-absorbing rate at 20°C and 65% RH

$k_1$ : moisture-absorbing speed constant

$t$ : 0 to 30 minute(s)

$$W_2 = (W_a - W_b) (1 - e^{-k_2 t})$$

$W_2$ : moisture-absorbing rate at time  $t$  from  $W_b$

$W_a$ : saturated moisture-absorbing rate at 20°C and 30% RH

$W_b$ : saturated moisture-absorbing rate at 20°C and 80% RH

$k_2$ : moisture-desorbing speed constant

$t$ : 0 to 30 minute(s)

[Claims]

[Claim 1] A moisture-absorbing cross-linking acrylic fiber, characterized in that, a saturated hygroscopic rate at 20°C and 65% RH is 15 to 35% by weight, a hygroscopic speed constant  $k_1$  in the following rate equation is within a range of 0.015 to 0.029 and a moisture-desorbing speed constant  $k_2$  thereof is within a range of 0.005 to 0.015.

$$W_1 = W_e (1 - e^{-k_1 t})$$

$W_1$ : moisture-absorbing rate within the time  $t$  from absolute drying

$W_e$ : saturated moisture-absorbing rate at 20°C and 65% RH

$k_1$ : moisture-absorbing speed constant

$t$ : 0 to 30 minute(s)

$$W_2 = (W_a - W_b) (1 - e^{-k_2 t})$$

$W_2$ : moisture-absorbing rate at time  $t$  from  $W_b$

$W_a$ : saturated moisture-absorbing rate at 20°C and 30% RH

$W_b$ : saturated moisture-absorbing rate at 20°C and 80% RH

$k_2$ : moisture-desorbing speed constant

$t$ : 0 to 30 minute(s)

[Claim 2] The moisture-absorbing cross-linking acrylic fiber according to claim 1, wherein the fiber further has adjusting functions which are pH buffering property, flame retarding property, antibacterial property, deodorizing property, anti-pilling property, antistatic property, water-sucking property and easily drying property.



[Claim 3] The moisture-absorbing cross-linking acrylic fiber according to claim 1 or 2, wherein a cross-linking structure is introduced into an acrylic fiber by means of a hydrazine treatment so that an increase in the content of nitrogen is adjusted to a range of from 1.0 to 8.0% by weight, hydrolysis is carried out so that carboxyl group is introduced into 1.0 to 5.0 meq/g of the amount of residing nitrile group while amide group is introduced into residual portion and then 50 to 90 mol% of the carboxyl group is made into a salt of one or more metal(s) selected from the group consisting of Mg, Ca, Cu, Zn, Al, Ag and Fe in which a hot-air temperature of the final thermal treatment conducted is 100 to 230°C.

[Claim 4] A fiber structure which is characterized by containing not less than 10% by weight of the moisture-absorbing cross-linking acrylic fiber mentioned in any of claims 1 to 3.

[Detailed Description of the Invention]

[0001]

[Technical Field of Invention]

The present invention relates to a temperature-adjusting and moisture-adjusting highly moisture-absorbing fiber where the speeds of absorption and desorption of moisture are controlled in which the fiber has adjusting functions such as pH buffering property, flame retarding property,

antibacterial property, deodorizing property, anti-pilling property, antistatic property, water-retaining property, water-sucking property and easily drying property and is equipped with health, pleasance, safety, hygiene and easy care properties. Also, the invention relates to a fiber structure containing the fiber, and products using the fiber structure contributes to providing a comfortable living environment by the above mentioned functions.

[0002]

[Prior Art]

There have been expected highly functional composite materials having all functions of health, comfort, safety and hygiene so as to be able to cope with the present days where living environments such as airtightness and air conditioning, aging society and living cultures are developing and increasing. Corresponding to the above, progresses in sciences for consumption of fiber products concerning human functions and comfort for wear are significant. Moisture is always evaporated from human body and sweating is resulted during hot time upon physical exercises and in putting on clothing or bedclothes with low air permeability and, as a result, moisture in clothing and bedclothes becomes high causing a sweating feel. On the other hand, when one puts on a clothing having poor moisture absorbing rate or a clothing having quick moisture absorbing and desorbing speeds even in case its moisture

absorbing rate is high, cooling feel or hot feel is apt to happen against changes in the environment such as coming into and going out from air-conditioned rooms. It has been also well known that, when the bedclothes as such are put on, one feels uncomfortable feeling such as poor temperature-keeping property or, even if the temperature-keeping property is available, cooling feel early in the morning. As to the moisture-absorbing fiber, there have been used natural fibers such as cotton and wool, regenerated fibers such as rayon and semi-synthetic fibers such as acetate fiber. On the other hand, in the case of synthetic fibers having poor moisture-absorbing property, fibers having fine hollows and grooves are recently available as a result of development of technology and devices have been carried out for overcoming the disadvantages in the conventional synthetic fibers (refer, for example, to Japanese Patent Laid-Open Nos. 57/051,812 and 03/161,506). However, although those fibers have excellent water-sucking speed and water-retaining property, their moisture-absorbing rate is poor whereby they do not well satisfy the function of adjusting the temperature and the humidity in the clothing.

[0003] On the other hand, there has been a proposal for a moisture-absorbing and moisture-desorbing cross-linking acrylic fiber which takes moisture in the air and is able to be regenerated (Japanese Patent Laid-Open No. 05/132,585) where Examples therein shows that its saturated

moisture-absorbing rate at 20°C and 65% RH reaches as high as 55% and quick moisture-absorbing and desorbing rate is emphasized as its characteristic. However, although this fiber is excellent in heat generation by adsorbed heat and in moisture-desorbing ability, its moisture-absorbing ability and moisture-desorbing ability are too high and, therefore, when it is used in clothing and in bedclothes contacting human body, a disadvantage where the moisture-keeping property of the skin surface is lost is predicted.

[0004]

[Problems that the Invention is to Solve]

The present invention has been created in order to solve the problems in the conventional art as such and its object is to provide a moisture-absorbing cross-linking acrylic fiber having temperature-adjusting and moisture-adjusting functions which appropriately adjust the temperature and the humidity in the clothing. Further object of the present invention is to provide a moisture-absorbing cross-linking acrylic fiber equipped with health, comfort, safety, hygiene and easy care properties having harmonizing functions such as pH buffering property, flame retarding property, antibacterial property, deodorizing property, anti-pilling property, antistatic property, water-retaining property, water-sucking property and easily drying property and also to provide a fiber structure containing the fiber.

[0005]

[Means for Solving the Problems]

In order to achieve the above-mentioned objects, the present inventors have conducted intensive investigations and, as a result, they have accomplished the present invention. Thus, the present invention relates to a moisture-absorbing cross-linking acrylic fiber, characterized in that, a saturated hygroscopic rate at 20°C and 65% RH is 15 to 35% by weight, a hygroscopic speed constant  $k_1$  in the following rate equation is within a range of 0.015 to 0.029 and a moisture-desorbing speed constant  $k_2$  thereof is within a range of 0.005 to 0.015.

$$W_1 = W_e (1 - e^{-k_1 t})$$

$W_1$ : moisture-absorbing rate within the time  $t$  from absolute drying

$W_e$ : saturated moisture-absorbing rate at 20°C and 65% RH

$k_1$ : moisture-absorbing speed constant

$t$ : 0 to 30 minute(s)

$$W_2 = (W_a - W_b) (1 - e^{-k_2 t})$$

$W_2$ : moisture-absorbing rate at time  $t$  from  $W_b$

$W_a$ : saturated moisture-absorbing rate at 20°C and 30% RH

$W_b$ : saturated moisture-absorbing rate at 20°C and 80% RH

$k_2$ : moisture-desorbing speed constant

$t$ : 0 to 30 minute(s).

[0006] In addition to the above temperature-adjusting

and moisture-adjusting functions, the moisture-absorbing cross-linking acrylic fiber in accordance with the present invention also has harmonizing functions which are pH buffering property, flame retarding property, antibacterial property, deodorizing property, anti-pilling property, antistatic property, water-sucking property and easily drying property.

[0007] The moisture-absorbing cross-linking acrylic fiber having the above various functions is able to be achieved by such a manner that a cross-linking structure is introduced into an acrylic fiber by means of a hydrazine treatment so that an increase in the content of nitrogen is adjusted to a range of from 1.0 to 8.0% by weight, hydrolysis is carried out so that carboxyl group is introduced into 1.0 to 5.0 meq/g of the amount of residing nitrile group while amide group is introduced into residual portion and then 50 to 90 mol% of the carboxyl group is made into a type of one or more metal(s) selected from the group consisting of Mg, Ca, Cu, Zn, Al, Ag and Fe in which a hot-air temperature of the final thermal treatment conducted is 100 to 230°C. The present invention further relates to a fiber structure containing not less than 10% by weight of the above moisture-absorbing cross-linking acrylic fiber.

[0008] The present invention will now be illustrated in detail as follows. The moisture-absorbing speed constant is determined by the following rate equation [I] proposed by Niwa



and Nosaka [*Senshoshi*, 5, 73 (1964)].

$$[I] \quad W = W_e (1 - e^{-kt})$$

W: moisture-absorbing amount at the time t

$W_e$ : equilibrated moisture-absorbing amount

k: moisture-absorbing speed constant

According to the above paper, the moisture-absorbing speed constant k is large in the case of a synthetic fiber with low moisture-absorbing property and is  $0.153 \text{ mm}^{-1}$  and  $0.173 \text{ mm}^{-1}$  in acrylic and polyester fibers, respectively while it is  $0.032 \text{ mm}^{-1}$  and  $0.078 \text{ mm}^{-1}$  in rayon and acetate, respectively. In the case of moisture-absorbing natural fiber such as cotton and wool, it is  $0.043 \text{ mm}^{-1}$  and  $0.040 \text{ mm}^{-1}$ , respectively and the moisture-absorbing speed constant calculated from the formula [I] by the present inventors is  $0.12 \text{ mm}^{-1}$  for acrylic fiber,  $0.13 \text{ mm}^{-1}$  for polyester,  $0.06 \text{ mm}^{-1}$  for cotton and  $0.04 \text{ mm}^{-1}$  for wool and they are almost identical with the above data. The present inventors have found that the saturated moisture-absorbing rate of the fiber and moisture-absorbing and moisture-desorbing speeds thereof are related to temperature-adjusting and moisture-adjusting properties in clothing or bedclothes and are closely related to comfortableness in wearing and moisture-keeping property on the skin surface. Thus, in the case of highly moisture-absorbing fiber where the saturated moisture-absorbing rate at  $20^\circ\text{C}$  and 65% RH is 15 to 35% by weight

and the moisture-absorbing and moisture-desorbing speed constant is controlled to a specific range of less than that of cotton, it is possible to maintain comfortable clothing and environment in bedclothes being excellent in a moisture-adjusting property against the change in the temperature and the humidity in the environment.

[0009] In the present invention, a saturated moisture-absorbing rate at 20°C and 65% RH is 15 to 35% by weight and the moisture-absorbing speed constant  $k_1$  and the moisture-desorbing speed constant  $k_2$  in the above-mentioned rate equation are within a range of from 0.015 to 0.029 and from 0.005 to 0.015, respectively whereby the aimed temperature-adjusting and moisture-adjusting properties are able to be achieved. As to a method for adjusting the saturated moisture-absorbing rate at 20°C and 65% RH to 15 to 35% by weight, a method where 50 to 90 mol% or, preferably, 60 to 85 mol% of the amount of carboxyl group is made into a form of a salt of one or more metal(s) selected from the group consisting of Mg, Ca, Cu, Zn, Al, Ag and Fe is able to be adopted. When the range is out of the above, the aimed moisture-absorbing level is unable to be achieved. On the other hand, although the fiber prepared by that method has a moisture-absorbing speed constant which is similar to that of the natural fiber, the object of the present inventors that the moisture-absorbing speed constant and the moisture-desorbing speed constant are to be

controlled within a range of from 0.015 to 0.029 and from 0.005 to 0.015, respectively is able to be achieved when the hot-air temperature during the final treatment is made at 100 to 230°C or, preferably, 110 to 210°C. When the temperature in the final treatment is lower than the lower limit, tight structure of the fiber surface is not formed yet and the moisture-absorbing and desorbing speed constants become large. When it is higher than the upper limit, it is not preferred in view of coloration and lowering in the strength of the fiber.

[0010] The present invention mainly comprises a cross-linking acrylic fiber where a cross-linking structure is introduced into an acrylic fiber by means of a hydrazine treatment so that an increase in the content of nitrogen is adjusted to a range of from 1.0 to 8.0% by weight or preferably from 3.0 to 8.0% by weight, hydrolysis is carried out so that carboxyl group is introduced into 1.0 to 5.0 meq/g or preferably 2.5 to 5.0 meq/g of the amount of residing nitrile group while amide group is introduced into residual portion and then 50 to 90 mol% or preferably 60 to 85 mol% of the carboxyl group is made into a salt of one or more metal(s) selected from the group consisting of Mg, Ca, Cu, Zn, Al, Ag and Fe. Accordingly, since the nitrile group is greatly changed as such, the fiber of the present invention is able to be said to be a cross-linking acrylic modified fiber. When an increase in the nitrogen amount in the fiber is less than the lower limit, although the

anti-pilling property is endowed, it is not possible to prepare the fiber having a property satisfying the processing property such as spinning and weaving while, when it is more than the upper limit, the aimed moisture-absorbing property, water-retaining property, water-sucking property and antistatic property are unable to be achieved. In the above, although metal salt is selected from the group consisting of Mg, Ca, Cu, Zn, Al, Ag and Fe, it is also possible to use other metal than the above so far as the balancing function of temperature adjustment and moisture adjustment of the present invention are not deteriorated. However, amount of such a metal is not more than 5 mol% in terms of a carboxyl group amount.

[0011] With regard to a method where nitrile group which is not subjected to a hydrazine cross-linking by a hydrolyzing reaction but remains therein is substantially diminished and an amide group is introduced into 1.0 to 5.0 meq/g of carboxyl portion, there may exemplified a method where a heating treatment is conducted under the state in which a basic aqueous solution of alkali hydroxide, ammonia, etc. or an aqueous solution of mineral acid such as nitric acid, sulfuric acid or hydrochloric acid is impregnated or a material fiber is dipped in the aqueous solution. It is also possible to carry out a hydrolyzing reaction together with the above introduction of the cross-linking bond. When the carboxyl group does not satisfy the above-mentioned lower limit, a moisture-absorbing

rate becomes low while, when it is more than the upper limit, a moisture-absorbing rate becomes too high whereby it is unable to adjust the climate in the clothing or, particularly, a moisture-keeping property onto the skin surface. Further, although an anti-pilling property is able to be endowed, property of the fiber for achieving the processing ability such as spinning property and weaving property is unable to be achieved as well.

[0012] As to a method of making a carboxyl group into a salt type, there may be advantageously used a method where the above-mentioned hydrolyzed fiber is dipped in an aqueous solution of various kinds of salt-type hydroxide or salt which will be exemplified below followed by washing with water and drying. With regard to the salt type of the carboxyl group hereinabove, it is necessary that 50 to 90 mol% is a salt type with one or more metal(s) selected from the group consisting of Mg, Ca, Cu, Zn, Al, Ag and Fe. When the range is lower than the above, a pH buffering property in an alkaline side is deficient and a cross-linking structure is insufficient whereby a deodorizing property to ammonia is lacking and the aimed adjusting function is unable to be achieved. On the other hand, when it is more than the above range, a pH buffering property in an acidic side is deficient, a drying speed becomes slow and easy care property lowers whereby the aimed adjusting function is unable to be achieved.

[0013] As such, it is now possible to provide an acrylic fiber having a saturated moisture-absorbing rate under 20°C and 65% RH and adjusting functions such as pH buffering property, flame retarding property, antibacterial property, deodorizing property, anti-pilling property, antistatic property, water-retaining property, water-sucking property and easily drying property as well as being equipped with health, comfort, safety, hygiene and easy care properties and also to provide a fiber product thereof. When there is further needed a necessity to enhance the tensile strength, it is recommended to choose a fiber having a high dichroic ratio as a starting acrylic fiber as will be mentioned later.

[0014] As to an apparatus for the manufacture of the above moisture-absorbing cross-linking acrylic fiber, a means where an acrylic fiber is charged in a container equipped with a pump circulating system and then the above-mentioned reactions for the introduction of the cross-linking bond, hydrolysis and formation of metal salt are successively carried out is preferred in view of safety, uniform reactivity, etc. A representative example of an apparatus therefor (a container equipped with a pump circulating system) is an Obermeyer dyeing machine of a compression type.

[0015] Further, in order to provide the aimed moisture-absorbing rate and temperature-adjusting and moisture-adjusting functions as well as adjusting functions



such as pH buffering property, flame retarding property, antibacterial property, deodorizing property, anti-pilling property, antistatic property, water-retaining property, water-sucking property and easily drying property together with a property necessary for spinning and weaving processes, it is particularly preferred to adopt a starting acrylic fiber having the following characteristics.

[0016] Thus, it is preferred to adopt an acrylic fiber where AN type polymer molecules forming the fiber are well oriented and a dichroic ratio by Congo Red (hereinafter, it will be referred to as CR) is not less than 0.4 or, more preferably, not less than 0.5. Incidentally, the CD dichroic ratio is determined by a method mentioned in *Kobunshi Kagaku*, 23(252), 193 (1966).

[0017] There is no limitation for a means of manufacturing the acrylic fiber as such and known means may be used appropriately so far as the above CR dichroic ratio is fulfilled. However, when a means where the total extension rate is not less than 4-fold or, preferably, not less than 8-fold and the step reducing rate is not more than 40% or, preferably, not more than 30%, it is able to manufacture the desired acrylic fiber in an industrial scale.

[0018] Further, when a fiber which is after elongation and before the heating treating (i.e., a fiber where a starting spinning solution of an AN type polymer is spun according to

a conventional method whereby, although subjected to an elongation orientation, no heating treatment such as drying for making tight and releasing treatment with moist heat is not carried out yet or, particularly, a water-swollen gel-form fiber after a wet spinning or a dry/wet spinning and elongation in which degree of swelling with water is 30 to 150%) is used as the starting acrylic fiber, dispersing property of the fiber and penetrating property of the fiber into the reaction solution are improved whereby introduction of the cross-linking bond and hydrolyzing reaction are able to be carried out uniformly and quickly and, therefore, that is preferred. Incidentally, degree of swelling with water is percentage of the water content expressed on the basis of dry fiber weight.

[0019] Examples of the form of the appearance of the fiber structure in accordance with the present invention are thread, yarn (including wrap yarn), filament, knitted thing, woven thing, nonwoven fabric, paper-shaped product, sheet-shaped product, laminated product and cotton-like product (including that in spherical and block forms) and also a product having an outer coat thereon. Examples of the form how the moisture-absorbing acrylic fiber of the present invention is contained in the structure are that it is distributed substantially uniformly by means of mixing with other materials, that it is made to concentratedly exist in any of layers (which

may be singular or plural) in case of the structure having plural layers and that it is distributed in each of the layers in a specific ratio.

[0020] Accordingly, there are quite a lot of fiber structures of the present invention as a result of combinations of the above-exemplified appearance forms and contained forms. Since the fiber of the present invention has many functions as mentioned already, it is appropriately decided what kind of structure is to be adopted by taking the mode of use of the final product (such as modification depending upon seasons; for sports or for inner clothing, internal clothing or outer clothing; curtain or carpet; bedclothes; utilization as cushion or insole or for air conditioners; etc.) into consideration and also by taking the required function, the contribution of the fiber of the present invention in expressing such functions, etc. into consideration.

[0021] Moreover, when the structure is observed carefully, there are many cases such as that the moisture-absorbing acrylic fiber of the present invention is merely used either solely or jointly in a mixed state with other material almost uniformly and that the fiber is layered or laminated with other material by means of sticking, adhesion, fusion, attaching, etc. to form a layered product having 2 to 5 plural layers. There is also a case where, although layered, no positive adhesion is carried out but the layered state is

maintained using a support.

[0022] Examples of the use of the final product utilizing the fiber structure of the present invention are, as mentioned above, that used by human by putting on, bedclothes such as mattress, pillow and cushion, interiors represented by curtain and carpet and others such as moisture adjustment and deodorization. In order to satisfy the demanded function depending upon the use as such, the optimum structure such as single layer, plural layers and application of outer coat thereon is selected.

[0023] As mentioned already, the fiber structure of the present invention contains not less than 10% by weight of the moisture-absorbing acrylic fiber of the present invention. Therefore, other materials such as fiber, synthetic rubber, rubber, resin and plastic are jointly used in an amount of not more than 90% by weight of the total fiber but, when the structure comprises the moisture-absorbing acrylic fiber only or, in other words, 100% by weight thereof, other material is not used together. Amount of the moisture-absorbing acrylic fiber of the present invention used is usually from 10% by weight to less than 100% by weight or, preferably, from 10% by weight to 50% by weight in case a structure is prepared by means of spinning by mixing with other fiber. When the amount is less than 10% by weight, even the moisture-absorbing acrylic fiber of the present invention is unable to achieve a sufficient

level of functions. The amount of the moisture-absorbing acrylic fiber of the present invention varies depending upon the use and, in the case of underwear or the like, it is 10 to 80% by weight or, preferably 10 to 70% by weight while, in the case of diaper or the like, it is at least 10% by weight or, preferably, not less than 20% by weight. With regard to a mode for the use, it is preferred to spin with other fiber to make into a spun yarn and to use as a fiber structure in a form of woven or knitted thing in the case of underwear. In the case of absorbing product such as diaper or sanitary goods or in the case of sportswear or the like, the moisture-absorbing acrylic fiber of the present invention is used either solely or together with other fiber to make into a web sheet followed by layering the sheet with other fiber sheet or woven/knitted thing. In order to actively utilize the characteristic of the moisture-absorbing acrylic fiber of the present invention, it is recommended to use a structure where the sheet of the present invention is applied to the side contacting the skin.

[0024] The reason why other material is used together as such is that it is useful for further enhancing the functions of the structure. Thus, although the moisture-absorbing acrylic fiber of the present invention has many functions as mentioned already, it is now possible to enhance the so-called fashionability such as that further high functions are endowed, preferred texture is endowed or fresh dyeing is available when

being made into a structure where other material is used together. An effect of improving the processing ability such as for mixed spinning is also able to be expected.

[0025] There is no particular limitation for other fiber which is able to be used together in the fiber structure of the present invention but publicly known ones such as natural fiber, organic fiber, semi-synthetic fiber and synthetic fiber may be used and, in some uses, inorganic fiber, glass fiber, etc. are also able to be adopted. In addition, the material which is able to be used together is not limited to fiber but, as mentioned already, it is also possible to adopt plastic, rubber, etc. for laminating to a film or for embedding into a film. Examples of the particularly preferred other fiber are natural fiber such as wool and cotton and synthetic fiber such as polyester, polyamide and polyacrylate as well as rayon and polynosic fiber.

When the moisture-absorbing cross-linking acrylic fiber of the present invention is used as a nonwoven fabric which is one of the frequently adopted structures, it is able to be used by making into a short fiber followed by appropriately mixing with cellulose fiber, pulp, synthetic fiber, etc. In such a use where a dimensional stability is particularly demanded, a nonwoven fabric comprising the fiber of the present invention and a thermally adhering fiber (preferably in a mixing ratio of 10 to 80% by weight) is recommended. With

regard to the thermally adhering fiber, anything may be used so far as it has a thermal adhering property and its examples are fibers comprising low- and high-melting components such as polyethylene-polypropylene, polyethylene-polyester and polyester-polyester. The nonwoven fabric using the fiber of the present invention is friendly to the skin in contacting the human body and is suitable for such a use where a water-absorbing property is to be achieved. For example, it is useful in a use as a diaper and is able to be used not only as a top sheet of nonwoven fabric of a diaper but also as a back sheet or even a diaper cover whereby the using amount of a highly water-absorbing polymer is able to be reduced. Since the fiber of the present invention is highly water-absorbing and also has an antibacterial property, the structure as such using the fiber has such advantages that it does not cause sweatiness, rash, etc. even when used for a long period of time.

[0026]

[Actions]

The reason why the moisture-absorbing acrylic fiber in accordance with the present invention has temperature-adjusting and moisture-adjusting functions together with various kinds of adjusting functions will be presumed mostly to be as follows.

[0027] Thus, although the fiber of the present invention starts from an AN type polymer, nitrile group substantially

disappears and, therefore, it is likely that the side chain bonding to the polymer chain is a salt-type carboxyl group produced by the hydrolyzing reaction of nitrile group with a cross-linking structure containing nitrogen produced by the reaction with hydrazine.

[0028] It has been known already that, usually, a base of the salt-type carboxyl group has a moisture-absorbing property and that, upon absorption of moisture, there are resulted hydrogen bond, heat of dissolution and heat generation participating in van der Waals force (adsorption heat). It is presumed that, at that time, as a result of the balance among univalent metal salt, di- and higher valent metal salt and carboxylic acid which is not a salt type, the aimed hygroscopic rate is designed and, further, a moisture-adsorbing and desorbing curve has more hysteresis as compared with the case of common moisture-absorbing fiber such as cotton, wool and rayon (refer to Fig. 6). On the other hand, when hot-air temperature in the final thermal treatment is raised and tightness of the fiber surface is enhanced, a synergism with the above hysteresis is generated whereby the moisture-absorbing speed constant in the initial stage is controlled to be low. It is likely that they result in the temperature-adjusting and moisture-adjusting functions.

[0029] The reason why the carboxyl groups in the specific ratio between a metal salt type and H type show a buffering



property to a weak acidity is that weakly basic metal salt and weak acid are appropriately existing together. In addition, the flame retarding property is presumed to be due to a cross-linking structure, acrylamide and metal salt while the antibacterial property is presumed to be resulted by the cross-linking structure. The antistatic property results in an effect that the moisture in the fiber leaks the generated static electricity and it is likely that the anti-pilling property is due to a low strength while the high moisture-absorbing property is due to a cross-linking structure and a salt-type carboxyl group. Further, the reason why spinning and knitting/weaving properties are maintained in spite of low strength will be greatly due to the orientation structure noted in the CD dichroic ratio and to intramolecular and intermolecular ionic cross-linking by the polyvalent metal.

[0030]

[Examples]

The present invention will now be more specifically illustrated as hereunder although the present invention is not limited thereto. The terms part(s) and percentage used in the Examples are those on the basis of weight unless otherwise mentioned.

[0031] Incidentally, pH buffering ability ( $\mu\text{eq/g}$ ), amount of total carboxyl group, amount of metal salt carboxyl

group, amount of H-type carboxyl group (meq/g), LOI (limiting oxygen index), moisture-absorbing rate, antibacterial property (difference between increased and decreased amounts), anti-pilling property (ICI grade), antistatic property (half-life time), water-sucking property (sucked-up amount), drying time, water-retaining rate, deodorizing property, moisture-absorbing speed constant, moisture-desorbing speed constant and regenerated amount of heat were measured by the following methods.

[0032] (1) pH buffering ability ( $\mu\text{eq/g}$ )

Well-dried fiber to be tested (0.4 g) was precisely weighed (X gram), 200 ml of water was added thereto, a 0.1N aqueous solution of hydrochloric acid or a 0.1N aqueous solution of sodium hydroxide was dropped thereinto, amount (Y cc) of the aqueous hydrochloric acid solution or the aqueous sodium hydroxide solution which was consumed until the pH reached 5.0 (in the case of the hydrochloric acid solution) or 7.0 (in the case of the sodium hydroxide solution) was measured and the buffering ability to an acid or to an alkali was calculated from the following formula.

$$\text{pH buffering ability } (\mu\text{mq/g}) = 1000 Y / X$$

[0033] (2) Total amount of carboxyl group (meq/g)

Well-dried fiber to be tested (about 1 g) was precisely weighed (X gram(s)), 200 ml of a 1N aqueous solution of hydrochloric acid was added thereto and the mixture was allowed

to stand for 30 minutes and filtered through a glass filter followed by washing with water. Such a treatment with hydrochloric acid was repeated for three times and the filtrate was well washed with water until the pH of the filtrate became not lower than 5. After that, the sample was placed in 200 ml of water, pH was adjusted to 2 by addition of a 1N aqueous solution of hydrochloric acid and a titration curve was prepared by a conventional manner using a 0.1N aqueous solution of sodium hydroxide. Consumed amount (Y cc) of the sodium hydroxide solution was determined from the titration curve and the total amount of the carboxyl group was calculated using the following formula.

$$\text{Total carboxyl group amount (meq/g)} = 0.1 Y / X$$

[0034] (3) Amount of carboxyl group of a metal salt type (meq/g)

Well dried fiber to be tested was precisely weighed, subjected to an acid decomposition using a mixed solution of concentrated sulfuric acid and concentrated nitric acid according to the conventional method and the metal was quantified by means of an atomic absorption spectrophotometry by the conventional method, calculated as an amount of carboxyl group to which metal is bonded and expressed in terms of molar percentage to the total carboxyl group.

[0035] (4) Amount of H-type carboxyl group (meq/g)

Amount of H-type carboxyl group was calculated by the

following formula.

Amount of H-type carboxyl group = (Amount of total carboxyl group) - (Amount of metal salt carboxyl group)

[0036] (5) LOI

This was carried out according to a measuring method for the LOI stipulated in JIS 7201.

[0037] (6) Moisture-absorbing rate (%)

The fiber to be tested (about 5.0 g) was dried at 105°C for 16 hours using a hot-air drier to measure the dried weight (W1 grams). It was then placed for 24 hours in a constant-temperature and constant-moisture device adjusted at 20°C temperature and 65% relative humidity. Weight (W2 grams) of the moistened sample as such was measured. From the above results, a moisture-absorbing rate was calculated by the following formula.

Moisture-absorbing rate (%) =  $[(W2 - W1) / W1] \times 100$

[0038] (7) Antibacterial property

Microbe strain used for the test: *Staphylococcus aureus* IFO 12732

Test method: A suspension of the microbe to be tested in bouillon was added to a sterilized cloth in accordance with a method stipulated by the SEK (Association for Hygienic Processing of Fiber Products), living cell numbers after incubation in a tightly-closed container at 37°C for 18 hours were counted and the difference between the cell numbers (B)

in the cloth and the cell numbers (C) in the sample to the inoculated cell numbers (A) was calculated.

Increasing/Decreasing Value =  $\log C - \log A$

Difference in Increasing/Decreasing Value =  $(\log B - \log A) - (\log C - \log A)$

[0039] (8) Anti-pilling property

This was carried out in accordance with a method using an ICI type tester in a method A of a pilling test method for woven and knitted things stipulated in JIS L 1076.

[0040] (9) Antistatic property

This was carried out in accordance with a method for antistatic test for woven and knitted things stipulated in JIS L 1094.

[0041] (10) Water-absorbing property

Sucked-up length (cm) after 30 minutes from the initiation of the measurement was determined in accordance with a method B (Bylec method) for water absorbing speed in a test method for knitted goods stipulated in JIS L 1018.

[0042] (11) Drying time

A woven cloth sample (10 × 10 cm) was dipped for 1 hour in pure water and dehydrated for 2 minutes using a centrifugal dehydrating machine (manufactured by Kubota) at the revolution of 300 g. The water-containing sample prepared as such was placed in a Tensilon (type UTM-II-20) set in an atmosphere of 20°C and 65% RH, changes in weight of the sample and time were

measured and drying time was determined by means of touched feel.

[0043] (12) Water-retaining rate (%)

The fiber sample (5 g) was dipped in pure water, allowed to stand at  $30 \pm 5^{\circ}\text{C}$  for 3 hours and dehydrated using a centrifugal dehydrating machine (manufactured by Kubota) for 3 minutes at the revolution of 1,000 G. Weight (W3 grams) of the dehydrated sample as such was measured. After that, the sample was dried in a hot-air drying machine of  $90^{\circ}\text{C}$  until it was absolutely dried, the weight (W4 grams) of the resulting sample was determined and a water-retaining rate (%) was calculated by the following formula.

$$\text{Water-retaining rate (\%)} = [(W3 - W4) / W4] \times 100$$

[0044] (13) Deodorizing property for ammonia

A sample fiber (2 g) was placed in a Tedler bag and tightly sealed and 3 liters of air was introduced thereinto. After that, 400 ppm of ammonia (W5) was placed into the bag and allowed to stand at room temperature for 120 minutes and the concentration of ammonia (W6) in the bag was measured using Kitagawa's detector tube. In the meanwhile, 400 ppm of ammonia was placed in a Tedler bag in which no sample was placed, the concentration of ammonia (W7) was measured after 120 hours and the result was used as a blank test. From the above results, the deodorizing property for ammonia was calculated by the following formula.

Deodorizing property for ammonia (%) =  $[(W5 - W6) / W7] \times 100$

[0045] (14) Moisture-absorbing speed constant ( $k_1$ )

Knitted material of 5 × 20 cm was absolutely dried using a hot-air drier at 105°C and cooled down to 20°C in a desiccator. Then the material was placed in a constant-temperature and constant-humidity device controlled at 20°C and 65% RH (manufactured by Tabai; type LHL-112T) and a moisture-absorbing rate ( $W_1$ ) during 120 hours was continuously measured. The knitted material was placed for 24 hours more in the constant-temperature and constant-humidity device and the saturated moisture-absorbing rate ( $W_e$ ) was measured. A moisture-absorbing speed constant ( $k_1$ ) was calculated from the following rate equation.

$$W_1 = W_e (1 - e^{-k_1 t})$$

$W_1$ : moisture-absorbing speed within the time  $t$  from the absolute drying

$W_e$ : saturated moisture-absorbing rate at 20°C and 65% RH

$k_1$ : moisture-absorbing speed constant

$t$ : 0 to 30 minute(s)

[0046] (15) Moisture-desorbing speed constant ( $k_2$ )

A knitted material of 5 × 20 cm was placed for 24 hours in a constant-temperature and constant-humidity device controlled at 20°C and 80% RH and the saturated moisture-absorbing rate ( $W_b$ ) at that temperature and humidity

was measured. The knitted material was placed in a constant-temperature and constant-humidity device controlled at 20°C and 30% RH and the moisture-absorbing rate during storage for 120 minutes was ( $W_2$ ) measured. The knitted material was further placed in a constant-temperature and constant-humidity device controlled at 20°C and 30% RH for 24 hours and the saturated moisture-absorbing rate ( $W_a$ ) at 20°C and 30% RH was measured. The moisture-desorbing speed constant ( $k_2$ ) in the following rate equation was calculated.

$$W_2 = (W_a - W_b)(1 - e^{-k_2 t})$$

$W_2$ : moisture-absorbing rate at time  $t$  from  $W_b$

$W_a$ : saturated moisture-absorbing rate at 20°C and 30% RH

$W_b$ : saturated moisture-absorbing rate at 20°C and 80% RH

$k_2$ : moisture-desorbing speed constant

$t$ : 0 to 30 minute(s)

[0047] (16) Regenerated amount of heat (°C·hr)

A sample fiber (2.5 g) subjected to carding and absolute drying was filled in a bag made of polyester cloth of 4.5 cm diameter and 6.0 cm length and a temperature detector was inserted into its center. The sample was hung in a constant-temperature and constant-humidity device controlled at 20°C and 90% RH and the temperature in the cloth was continuously recorded automatically. An increased temperature to an environment temperature for 0 to 1 hour was integrated and was defined as a regenerated amount of heat



(°C·hr).

[0048] Example 1

An acrylonitrile polymer comprising 90% of acrylonitrile and 10% of methyl acrylate was dissolved in a 48% aqueous solution of sodium rhodanate and the resulting original solution for spinning was subjected to spinning, washing with water, extending, crimping and heating by conventional means to give a material fiber of 0.8 denier x 70 mm. To 1 kg of this material fiber was added 5 kg of 30% by weight hydrazine hydrate followed by subjecting to a cross-linking treatment at 98°C for 3 hours. An increasing amount of nitrogen was 5.0%. The cross-linking fiber was washed with water, 5 kg of 3% by weight of sodium hydroxide was further added thereto and hydrolysis was conducted at 90°C for 2 hours. After that, a treatment with 1N aqueous solution of HNO<sub>3</sub> was carried out to convert a carboxyl group to an H-type followed by washing with water, pH was adjusted to 6.5 with 1N NaOH, 50 g of calcium chloride was added thereto and a metal-salt treatment was carried out at 60°C for 2 hours. After well washing with water, there were carried out dehydration, treatment with oil and thermal treatment as shown in Table 1 to give a cross-linking acrylic fiber. Carboxyl group in the fiber and Ca-type carboxyl group in the total carboxyl group were 4.3 meq/g and 80 mol%, respectively.

[0049] Characteristics of the resulting fiber are shown

in Table 1. Moisture-absorbing rates of the fibers Nos. 1 to 3 of the present invention are 25 to 28% and are as high as about 3.5-fold of cotton. Moisture-absorbing speed curves under the atmosphere of 20°C and 65% RH and moisture-desorbing speed curves are shown in Fig. 1 and Fig. 2, respectively. Moisture-absorbing speed constant  $k_1$  and moisture-desorbing speed constant  $k_2$  determined from those curves during the initial 0 to 30 minute(s) are shown in Table 1 and there is clearly shown a tendency that, when temperature at the final thermal treatment is raised,  $k_1$  and  $k_2$  lower. On the other hand, adsorption heat generating and heat releasing curves of the temperature in the fiber at 20°C and 65% RH are shown in Fig. 3. As will be apparent from Fig. 3, all fibers generate the heat by endothermy as a result of moisture absorption and, since a fiber having big  $k_1$  quickly finishes the adsorption heat generating reaction, its cooling time down to the atmospheric temperature is short while, in the fiber of the present invention, since adsorption heat generation endures as a result of the effect of small  $k_1$ , a cooling speed as a result of heat release is slow. Thus, the temperature in the fiber after 60 minutes is higher to an extent of about +4°C or about +3°C for cotton or wool, respectively and, in addition, the amount of regenerated heat during 0 to 60 minute(s) which is a yardstick for a temperature-retaining property is not less than 2-fold of cotton and not less than 1.5-fold of wool. From those

results, it is proved that the saturated moisture-absorbing rate and  $k_1$  greatly affect the heat generating amount and heat regenerating amount. Moreover, the water-retaining rate of the fiber of the present invention shows a level of as high as cotton. On the other hand, the LOI value which is a yardstick for a flame retarding property is as high as 29 to 30 and, even when ignited with a match, no burning happens at all. Further, a deodorizing rate for ammonia is as high as not lower than 95% and it is found to have a high deodorizing function to ammonia.

[0050]

[Table 1]

Examples	Fiber No.	Temperature for thermal treatment (°C)	Moisture absorbing rate (%)	Regenerated amount of heat (°C hr)	Moisture absorbing speed constant $k_1$ (mm <sup>-1</sup> )	Moisture desorbing speed constant $k_2$ (mm <sup>-1</sup> )	pH buffering property (μmole/g acid alkali)	Water retaining rate (%)	Flame retarding property (LOI)	Deodorizing rate for ammonia (%)
Example 1 of the present invention		120	28	6.1	0.020	0.010	1800 260	47	30	98
Example 2 of the present invention		200	25	6.0	0.015	0.003	1200 400	47	29	95
Example 3 of the present invention		150	27	6.5	0.018	0.007	1400 350	47	29	99
Comparative Example - cotton		---	7	2.6	0.035	0.060	200 0	45	17	—
Comparative Example - wool		---	12	3.0	0.065	0.020	260 0	35	23	---
Comparative Example - acrylic		---	1.5	0.3	0.117	0.090	260 0	15	18	17
Comparative Example - polyester		---	0.3	0.2	0.132	0.042	200 0	10	21	—

Cotton - combed one

Acrylic - Exlan KR-1.5<sup>d</sup> 51 mm (acrylic fiber)

[0051] Example 2

The fiber No. 3 (1.8<sup>d</sup> × 48 mm) prepared in Example 1 of the present invention was subjected to mixed spinning, carding, drawing and raw spinning by a conventional means with an acrylic fiber (Exlan; 1.5<sup>d</sup> × 51 mm) and a combed cotton together with

changing their mixed spinning ratio whereupon a yarn of 1/52 m count and twisted numbers of 830 T/M was prepared. As comparative examples, yarns were similarly prepared from acrylic fiber, cut wool, combed cotton and polyester fiber (Toyobo; 1.5<sup>d</sup> × 51 mm). After that, the yarns were treated with a smooth knitting machine of 20 gauges to prepare a knitted thing of basis weight of 200 ± 20 g/m<sup>2</sup>. After that, the knitted thing was scoured using a rotary bag dyeing machine, dried and made into knitted material samples A to F using a Hofmann setting machine. Details and characteristic values of the knitted material samples A to F are shown in Table 2. The knitted material A-1 using 100% of the fiber of the Example of the present invention reproduced antibacterial property, deodorizing property, LOI value, moisture-absorbing rate and pH buffering property in the same level as those of the original cotton fiber measured in Table 1. The anti-pilling property was in class 5 and no fuzzy ball was generated at all. The antistatic property was in the same level as in cotton where the half-life was one second. Water-sucking length was about 1.2-fold of that of cotton. Water-retaining rate was in the same level as that of cotton and, in spite of the fact that the moisture-absorbing rate was as big as about 3.5-fold of that of cotton, drying time by means of the feel by touching was as quick as not less than 3-fold of that of cotton and it was found to have an easy care property that hydrophilic

property is available, drying is quick and moistened feel is not little. On the other hand, in the case of a mixed-spun product of the fiber of the present invention example with acrylic fiber or cotton, although the lowering in LOI value is big to a mixed spun rate and a flame retarding effect is small, the same or even better results as the converted value for mixed spinning are achieved for other properties, i.e., antibacterial property, deodorizing property, anti-pilling property, antistatic property, pH buffering property and drying speed. The particularly good effect achieved is a synergism that the water sucking speed is quicker when an acrylic fiber is mixed and it suggests the possibility that capillary speed is accelerated and an effect by mixed spinning is high when not only an acrylic fiber but also a hydrophobic fiber such as polyester fiber is mixed followed by spinning. As such, the fiber of the present invention was proved to be able to provide multi-functional and epoch-making products in knitted thing for clothing represented by underwear, sweater, lingerie, brassiere, sweat suits, sports clothes, sweat shirt, leotard, gloves, socks, supporters, tights and pajama.

[0052]

[Table 2]

Knitted samples	Fiber used (%)	Difference between increase and decrease in antibacterial cell numbers	Flame retarding property (LOI)	Deodorizing property to ammonia (%)	Anti-pilling property (CI) (class)	Antistatic half value life (seconds)	Moisture absorbing rate (%)	pH buffering property (μeq/g)		Water soaking length (mm)	Drying time (minutes)
								acid	alkali		
Example A-1 of the present invention	Example No. 3 of the present invention = 100	6.4	28	99	5	1	27	1600	320	145	70
Example A-2 of the present invention	Example No. 3 of the present invention / acrylic = 60/40	6.0	22	99	4	5	15	1550	320	170	55
Example A-3 of the present invention	Example No. 3 of the present invention / acrylic = 30/70	4.7	20	93	3	14	8	1520	300	96	50
Example B of the present invention	Example No. 3 of the present invention / cotton = 30/70	3.6	19	97	6	1	18	1290	240	150	120
Comparative Example C	Cotton = 100	0.4	17	—	4	1	7	200	0	120	240
Comparative Example D	Wool = 100	0.3	23	—	2	60	10	250	5	5	70
Comparative Example E	Acrylic = 100	1.0	18	12	1	120<	2	250	0	100	40
Comparative Example F	Polyester = 100	0.8	21	—	1	120<	0.8	200	0	1	40

Cotton: combed one

Acrylic: Exlan KA-1.6/ 61 mm (acrylic fiber)

### [0053] Example 3

In order to more practically confirm the temperature-adjusting and moisture-adjusting effects of the knitted thing prepared in Example 2, each of three kinds of products which are the knitted thing of the example of the present invention and cotton (C) and acrylic (E) as knitted things for comparative example in a size of 10 cm × 10 cm was folded into two followed by being inserted with a sensor for temperature and humidity (THP-23 manufactured by Shin-ei K. K.) in the central part thereof, connected to a data stocker (TRH-DM3 manufactured by Shin-ei K. K.), placed in a constant-temperature and constant-humidity device (type LHL-1122T manufactured by Tabai Seisakusho) and continuously treated at the temperature and humidity of 20°C/80% RH and 20°C/30% RH with an interval of 60 minutes whereupon the

temperature and humidity in the woven cloth at that time were recorded. Changes in the humidity are shown in Fig. 4 while changes in the temperature are shown in Fig. 5. In an acrylic knitted thing where moisture-absorbing rate is low and moisture-absorbing and desorbing constants  $k_1$  and  $k_2$  are big, humidity changes almost proportional to the changes in the environment whereby no moisture-adjusting function is available at all. On the other hand, in the case of cotton which is a moisture-absorbing natural fiber, there is a tendency that the humidity in the fiber somewhat delays against the changes in the environment due to its moisture-absorbing and desorbing functions. On the contrary, in the fiber knitted thing of the example of the present invention, it was confirmed that changes in the humidity in the fiber against changes in the environment is small and a comfortable humidity of from about 50% RH to about 70% RH was maintained due to its characteristic that the moisture-absorbing rate is high and that the moisture-absorbing and desorbing constants  $k_1$  and  $k_2$  are low. With regard to the temperature in the fiber, there was almost no change at the environment temperature of 20°C in the case of an acrylic knitted thing while, in the case of cotton knitted thing, temperature rise of moisture-absorbing heat generation of 2 to 3°C was noted under high humidity while, when temperature lowered from high to low, heat of evaporation was taken away due to moisture desorption whereupon the

temperature lowered down to the environmental temperature of 20°C and that was identical with the phenomenon that cooling feel is noted upon putting on. Against the above, in the fiber of the example of the present invention, it was confirmed that the moisture-absorbing ability is high and the moisture-absorbing and moisture-desorbing speed constants  $k_1$  and  $k_2$  are small whereby the moisture-absorbing heat generating temperature is high and the retaining time at that temperature is also long and there are characteristics that the temperature-retaining property and the temperature-adjusting property are excellent.

[0054] Example 4

A mixed spun yarn A-3 comprising 30% of the fiber No. 3 of the example of the present invention prepared in Example 2 and 70% of acrylic and a yarn of 1/36 meter count of 100% acrylic yarn E were used to prepare each five Newmeyer blankets of  $1.65 \pm 0.05$  kg/sheet having basis weight pile length of 6 mm where both sides were napped. Each one blanket thereof was subjected to a destructive test while other four were provided to four panelists for a practically using test asking them to fill in the questionnaires. Results of the test are shown in Tables 3 and 4. The practically using test was carried out in winter between mid-January and late February and there was no restriction for the quilt and the sleeping mat therefor. The flame retarding property as shown in Table 3 was measured



after five washing treatments according to a method 103 of JIS L 0217 by a 45° methenamine test and a 45° tobacco test which are standards for the ability test for flame-retarding products. In the blanket using the knitted thing of A-3 of the present invention, the frictional electrification voltage which was not measured in the knitted thing of Example 3 was 3.0 KV and the half-life was lower than the knitted thing whereby a practical antistatic effect was confirmed. On the other hand, with regard to the effect of mixed spun yarn to the flame retarding property which was less effective in LOI of the knitted thing, the flame retarding effect of the blanket using the knitted thing of A-3 passed both of the 45° methenamine method and the 45° tobacco test. This is presumably due to a flame-retarding effect because of the fact that the condition is less severe as compared with a vertical method as in the case of knitted thing and that the present fiber does not show a behavior of fusion and burning as in the case of common synthetic fiber but is apt to be carbonized. With regard to the antibacterial property and the deodorizing property, nearly the same effect as in the knitted thing of Example 3 was available. In Table 4, nearly the common result of questionnaires is shown by the four panelists and the blanket using the knitted thing of A-3 of the present invention was confirmed to have a quickly warming property as compared with the blanket comprising 100% of acrylic which is usually used

in winter. Time from going into a bed until falling asleep is within about one hour for human and a quickly warming property is able to be expected as an effect of promoting a good sleep. With regard to other opinions, it was reported that no cooling feel was noted on the toes early in the morning. Since there is much perspiration on the toe, it is predicted that acrylic fiber having low moisture-absorbing property and quick moisture-absorbing and desorbing speed gives a cooling feel due to heat of evaporation caused by evaporation of moisture whereby that above result is well noticed as another characteristic of the fiber of the present invention. On the other hand, with regard to the opinion that the blanket using the fiber of the present invention showed a refreshing feel, it is presumed to be related to the moisture-adjusting effect of the knitted thing of Example 3 against the changes in temperature and experiments for practical use of blankets for spring and summer seasons will be quite interesting as well. Incidentally, for the sake of the reference, results of measurement of changes in temperature and humidity in the blankets of A-3 with lapse of time are shown in Fig. 7(a) and Fig. 7(b). As such, the fiber of the present invention was proved to be possible in preparing epoch-making commercial products having multiple functions in merchandizes for house decorations and bed goods mainly in pile products such as blankets, sheets, bedclothes and carpets.

[0055]

[Table 3]

Knitted thing No. used	Fibers used (%)			Flame retarding property		Antibacterial property	Deodorizing property
		Frictional electrification voltage (kV)	Half-life (seconds)	45° methanamine method	45° tobacco method	Difference in increasing and decreasing numbers of the cells	Deodorizing property to ammonia (%)
A-3	Example No. 3 of the present invention / acrylic = 30/70	3.0	1.8	carbonized length: 48 mm (passed)	neither residual flame nor residual dust was noted; passed	3.8	99
E	Acrylic = 100	5.8	1.2	carbonized length: 120 mm (failed)	both residual flame and residue dust were noted; failed	1.2	1.8

[0056]

[Table 4]

Knitted thing No. used	Fibers used (%)	Warm feeling upon use	Sweaty feel	Other opinions
A-3	Example No. 3 of the present invention / acrylic = 30/70	Quickly warming property was available and warmer than E	not noted	When the sample E was used, the toes felt a coolness early in the morning while, in the case of the sample A-3, no cooling feel was noted. The sample A-3 showed a refreshing feel as compared with the sample E and the blanket which has been used until now.
E	Acrylic = 100	Warm	not noted	

[0057] Example 5

30% Of the fiber No. 3 of the present invention ( $1.8^d \times 48$  mm) prepared in Example 1 and 70% of acrylic fiber (Exlan K8,  $1.5^d \times 51$  mm) were uniformly spun by mixing whereupon a 1/52 m count (twisted numbers: 700 T/M) was spun. Warps which were prepared by dyeing the above yarn using a package dyeing machine followed by pasting and warping using a paste mainly comprising PVA and woofs which were prepared by dyeing using a package dyeing machine without pasting were woven into a plainly woven tissue of warp density of 90 warps per inch and woof density of 70 woofs per inch using a high-speed weaving

machine, depasted and scoured and 0.3% by weight of a texture adjusting agent (such as an anionic softener) was adhered to the woven fabric followed by heating for 1 minute using a hot-air drier of hot-air temperature of 150°C to prepare a woven fabric sample with a basis weight of 120 g/m<sup>2</sup> which is a fiber structure of the present invention.

[0058] When the properties of the woven fabric samples prepared as such were evaluated, it was found that moisture-absorbing property, pH buffering property, anti-pilling property, antistatic property, deodorizing property to ammonia, antibacterial property and water-absorbing drying property were in the same degree of abilities as those of the knitted thing sample A-3 of Table 2. Such a woven fabric is well adaptable in the use for shirts. When design of the woven fabric is modified, the fabric is also able to be applied to clothing such as suits, trunks, scarves, mufflers and handkerchiefs and bedclothes such as sheets and ticking. A fiber structure by combining (by means of mixed spinning, mixed twisting or mixed weaving) with other materials is also suggested from the usefulness containing the fiber No. 3 of the example of the present invention.

[0059] Example 6

50% By weight of fiber No. 3 of the example of the present invention prepared in Example 1 (1.8<sup>d</sup> × 48 mm), 20% by weight of a thermally fused polyester fiber (2<sup>d</sup> × 51 mm) and 30% by

weight of an acrylic fiber (Exlan K8,  $1.5^d \times 51$  mm) were used for subjecting to a preliminary opening in a mixing machine and made into a needle punch cloth of 3 mm thickness and 600 g/m<sup>2</sup> basis weight using an apparatus where a raw cotton supplying lattice, a flat card, a card web laminating device and a needling device. After that, the resulting cloth was subjected to a thermal treatment for 60 seconds at 160°C and then passed through two calendar rollers set at 160°C at the rate of 10 m per minute to prepare a nonwoven fabric (A) of 2.5 mm thickness which is a fiber structure of the present invention.

[0060] Similarly was prepared a nonwoven fabric (C) of 2.5 mm thickness of comparative example using 80% by weight of acrylic fiber (Exlan K8;  $1.5^d \times 51$  mm) and 20% by weight of a thermally fused polyester fiber ( $2^d \times 51$  mm). A card web having a basis weight of 1/2 for the nonwoven fabric (A) and a card web having a basis weight of 1/2 for the nonwoven fabric (C) were layered on upside and downside, respectively and then subjected to the needling and thereafter under the same conditions to prepare a two-layered nonwoven fabric (B) of 2.5 mm thickness which is the fiber structure of the present invention. Those nonwoven fabrics (A), (B) and (C) were cut and sown to prepare insoles for shoes.

[0061] Three male adult panelists were selected and each of them was supplied with three sets of new shoes (made of

Kurarino, a synthetic leather) and each one set of insoles of (A), (B) and (C). Every week, both shoes and insoles were exchanged and a test was conducted for three weeks. Result of the test is shown in Table 5.

[0062]

[Table 5]

Nonwoven fabric samples	Insole products						Result of the using test (used for three weeks)		
	Weight (grams/foot)	Thickness (mm)	Moisture absorbing rate (%) at 20°C/85% RH	Water-sucking length (mm)	Difference in increase/decrease in antibacterial property	Deodorizing rate for ammonia (%)	Sweating feel	Wetting of the socks	Smell of the shoes
The present invention (A)	28.2	2.4	22.4	86	3.8	98.5	hardly noted	none	hardly smelled
The present invention (B)	28.0	2.4	22.0	98	6.2	99.8	not noted	none	hardly smelled
Comparative Example (C)	28.1	2.4	1.6	38	1.0	7.3	sweaty feel was noted	none	smelled

[0063] The insoles of (A) and (B) which are the fiber structures of the present invention had almost no sweaty feel as compared with the insoles (C) of the comparative example and, further, did not show any unpleasant feel due to wetting of the socks at all. Still further, smell of the shoes after use was very little whereby very comfortable property was available. This is due to the fact that the fiber structure comprising the fiber of the present invention has excellent moisture-absorbing rate and water-absorbing property and also has an excellent antibacterial property and the structure is well suitable for the use of insoles and coverings. In addition, by taking its characteristic of very high deodorizing rate for ammonia, the fiber structure of the present invention is able to be applied to goods for health and hygiene represented by

diaper cover, pad for incontinence, toiletries and filters as well as products for cleaning of water and air. Moreover, the fiber structure by modification of design for manufacturing method, mixing rate, mixing partner and combining method of the nonwoven fabric is also suggested by the usefulness of containing the fiber No. 3 of the present invention.

[0064] Example 7

Pile yarn comprising 100% of acrylic fiber (meter count 2/28" of a mixture containing Exlan K 691 [ $3^d \times 70$ ] and Exlan K 89 [ $3^d \times 64$ ] in 60/40 was dyed by a conventional method using a twisting dyeing machine and subjected to a softening treatment) and polyester yarn (Interlace 150 d/34 f) were used as raw yarns and woven by a conventional method using a knitting bore weaving machine and then subjected to dividing, polishing and cutting treatments to prepare a pile knitted fabric of 6 mm pile length and basis weight of 400 g/m<sup>2</sup>. On the other hand, 50% by weight of the fiber No. 3 ( $1.8^d \times 48$  mm) of the present invention prepared in Example 1 and 50% by weight of a hollow polyester fiber ( $3^d \times 51$  mm) were used and subjected to a preliminary opening using a cotton mixing machine followed by subjecting to a roller card to prepare a card web which is the fiber structure of the present invention. The web mixed with the fiber of the present invention was used as filling cotton to prepare a stuffed toy.

[0065] The above stuffed toy was provided to each of five

lady panelists and subjected to a using test by means of questionnaires and, as a result, there were found interesting properties such as that it becomes warm when held in arms and is comfortable, that it is comfortable when used as a substitute for a pillow and that it has a refreshing feel. This is presumably due to the contribution of the moisture-absorbing and heat generating properties of the fiber of the present invention via perceived or non-perceived sweat from the hand or the skin and it is understood that the product is well suitable in a fiber structure as interior cotton or stuffed cotton. Besides the above, the fiber structure of the present invention also has the functions of pH buffering property, antibacterial property, deodorizing property to ammonia, etc. whereby it is suggested that the structure is able to be utilized as interior cotton for bedclothes, interior cotton for pillows, interior cotton for cushions and interior cotton for antiperspirant pad.

[0066] Example 8

From the fiber No. 3 of the present invention, a card web sheet (A) of 100 g/m<sup>2</sup> basis weight and 3 mm thickness was prepared by the same method as in the case of the nonwoven fabric (A) of Example 6. A highly water-absorbing fiber sheet (C) in the same basis weight and thickness was prepared using a highly water-absorbing fiber (Ranshiru manufactured by Nippon Exlan Kogyo K. K.). Further, a water-absorbing polymer ((B)



comprising a partially cross-linking product of polyacrylic acid) and a gauze fabric (D) comprising 100% of cotton were prepared. They were layered in the order of D, A, B, C and D from the top to prepare a cross-stitch layered structure which is a fiber structure of the present invention. A 0.5% by weight aqueous solution of ammonia (4 cc) was absorbed with the upper side of the absorbing structure in a size of 5 cm<sup>2</sup>, then the structure was dipped in 100 cc of distilled water and pH was measured. The pH value was 6.5. Even after absorption of ammonia, there was no smell and the fact that the pH was stable as such shows that the product has an excellent buffering property.

[0067]

#### [Advantages of the Invention]

In accordance with the present invention, it is now possible to provide a temperature-adjustment and moisture-adjustment balanced fiber having many functions such as health, comfort, safety, hygiene and easy care properties or, in other words, a fiber having conditioning functions. The temperature-adjusting and moisture-adjusting functions of the present invention is able to be achieved if and when the saturated moisture-absorbing rate at 20°C and 65% RH is 15 to 35% by weight and moisture-absorbing and desorbing speed constant is within a specific range. In addition, the fiber of the present invention has nearly all adjusting functions

such as pH buffering property, flame retarding property, antibacterial property, antistatic property, deodorizing property, anti-pilling property, water-retaining property, water-sucking property and easy drying and, as compared with the conventional natural fibers and synthetic fibers, various significant functions are available. Moreover, the fiber of the present invention also has a significant effect of mixed spinning with various fibers and is able to be widely used in various processing and using fields.

[0068] Thus, due to cooperation with other partner material, a fiber structure containing not less than 10% by weight of the fiber of the present invention is able to well achieve the functions even when the using amount of the fiber of the present invention is small or is further able to achieve other functions whereby a lot of final products are provided.

[0069] Examples thereof are use as clothing contacting to the skin such as underwear, lingerie, pajama, clothing for suckling, girdle, brassiere, socks/stockings, tights, leotard and trunks and use as inner and outer clothing such as sweater, sweat shirts, suits, sportswear, scarf, handkerchief, muffler, artificial fur and clothing for suckling. Examples of the use as bedclothes and house decorations are floor covering such as carpet and mattress, blanket, curtain, bedclothes, sheets, interior cotton and filling cotton and examples of other uses are filter, adsorbent, supporter, stuffed toy, bandage,

styptic material and attachment for protection of wound. In order to actively utilize the excellent pH buffering property which is the characteristic feature of the fiber of the present invention, it is recommended to use the fiber as clothing contacting to the skin or as diaper, diaper cover, sanitary goods, etc.

#### Brief Description of the Drawings

Fig. 1 shows moisture-absorbing speed curves of various fibers.

Fig. 2 shows moisture-desorbing speed curves of various fibers.

Fig. 3 shows adsorption heat generating and heat releasing curves of various fibers.

Fig. 4 shows changes in humidity in the fiber with lapse of time.

Fig. 5 shows changes in temperature in the fiber with lapse of time.

Fig. 6 shows isothermal moisture-absorbing curves of fibers.

Fig. 7 shows changes in temperature in the blanket with lapse of time (a) and changes in humidity in the blanket with lapse of time (b).

Fig. 1

Fig. 1: Moisture-absorbing speed curves of various fibers

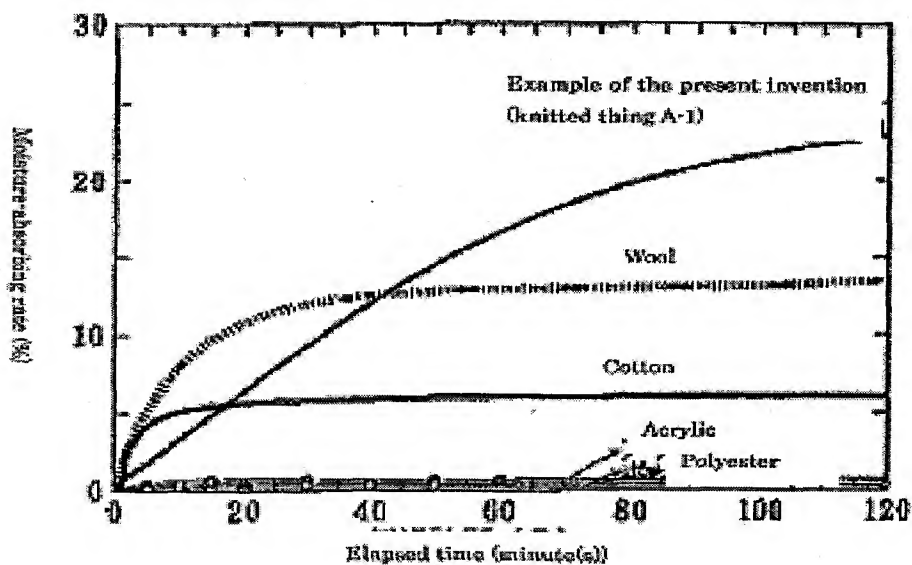


Fig. 2

Fig. 2: Moisture-desorbing speed curves of various fibers

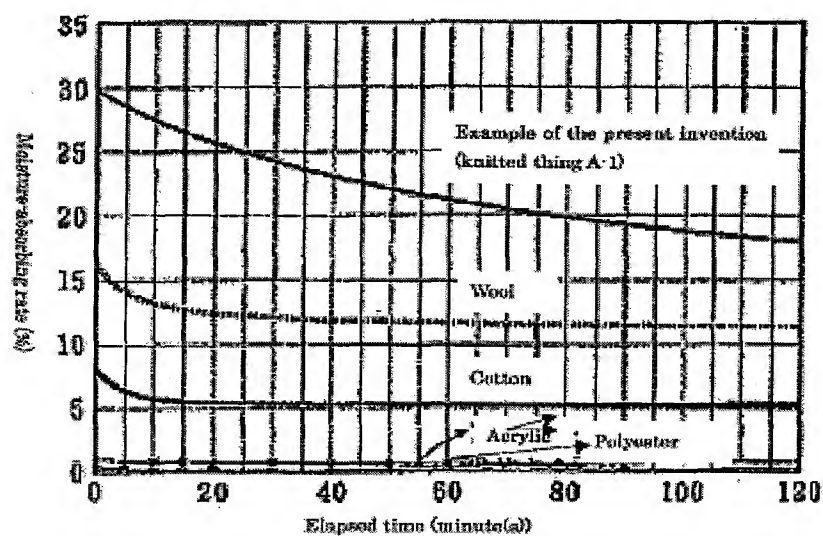


Fig. 3

Fig. 3: Adsorption heat-generating and heat-releasing curves of various fibers

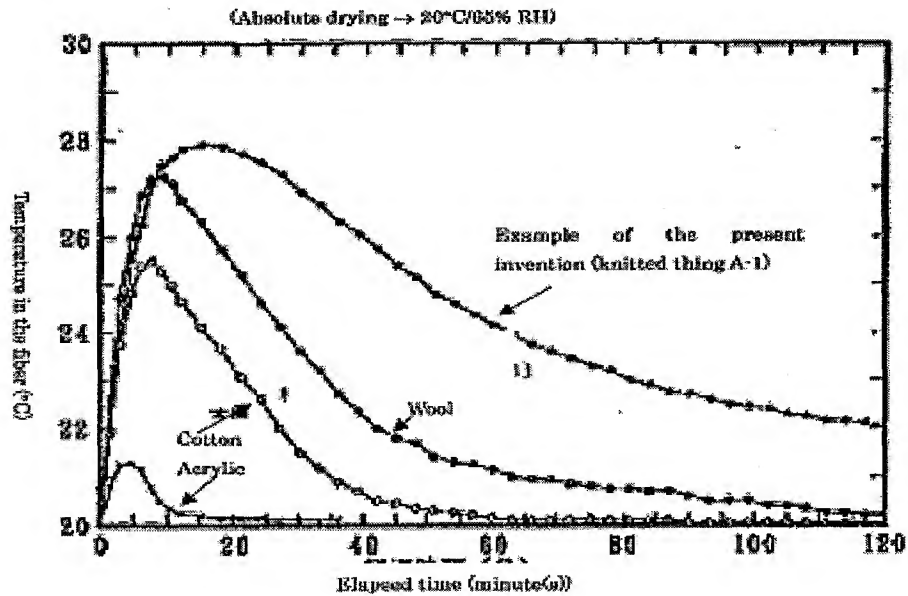


Fig. 4

Fig. 4: Changes in humidity in the fiber with elapse of time

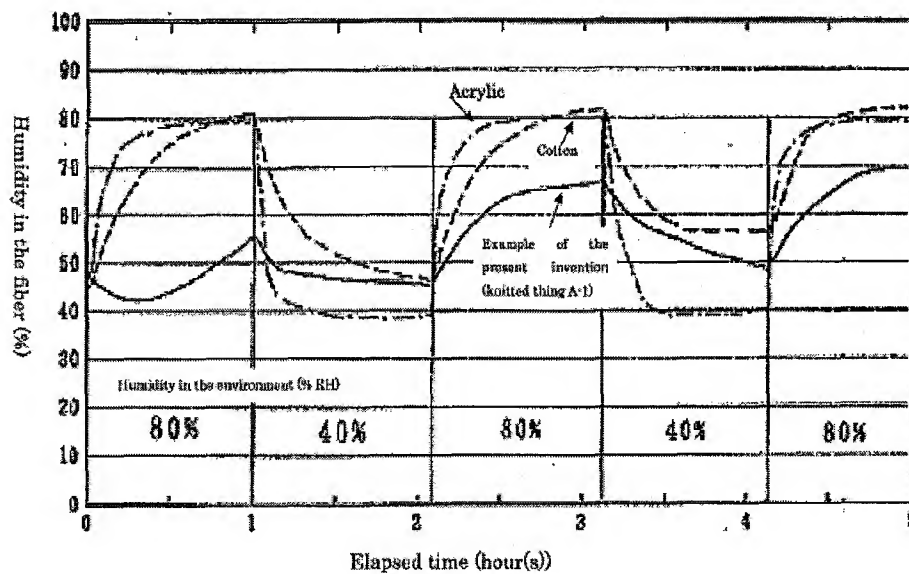


Fig. 5

Fig. 5: Changes in temperature in the fiber with elapso of time

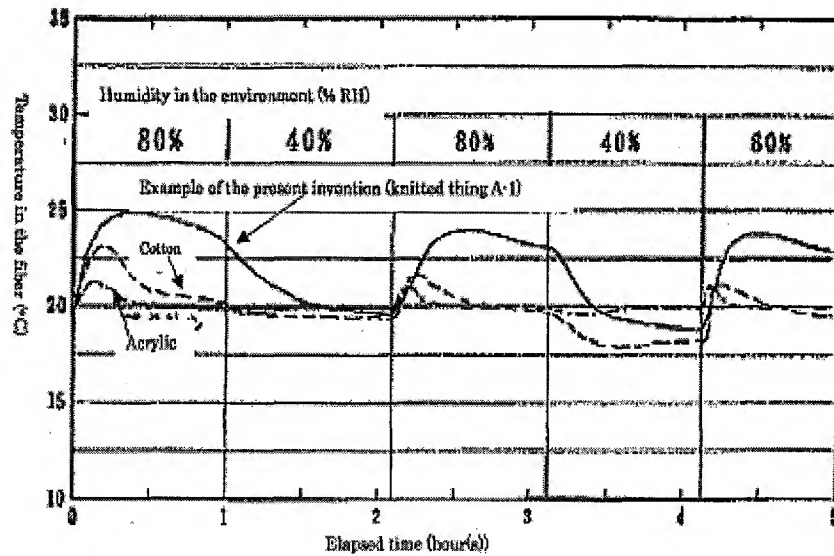


Fig. 6

Fig. 6: Isothermal moisture-absorption curves of fibers

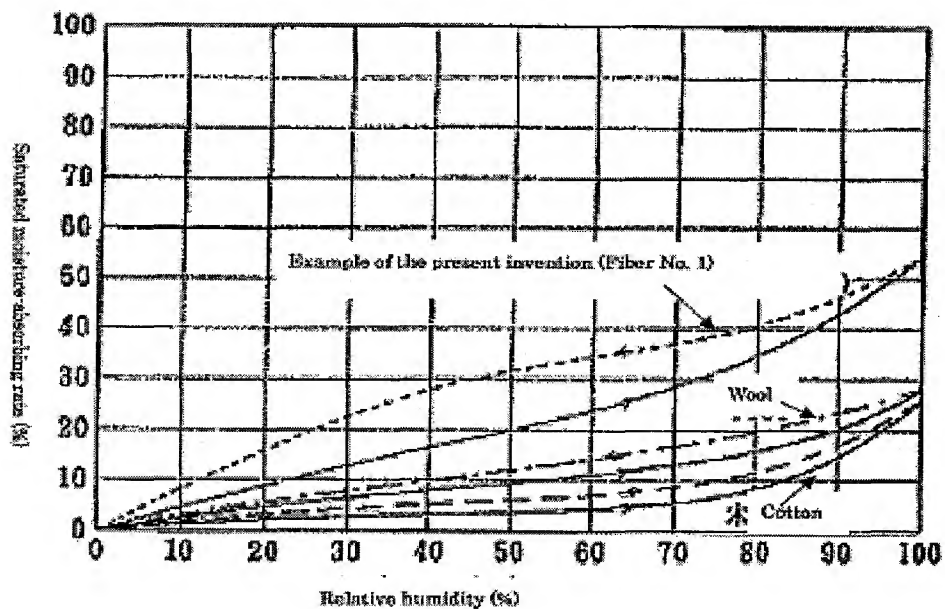


Fig. 7

Changes in temperature and humidity in bedclothes (blanket) with lapse of time

Fig. 7 (a)

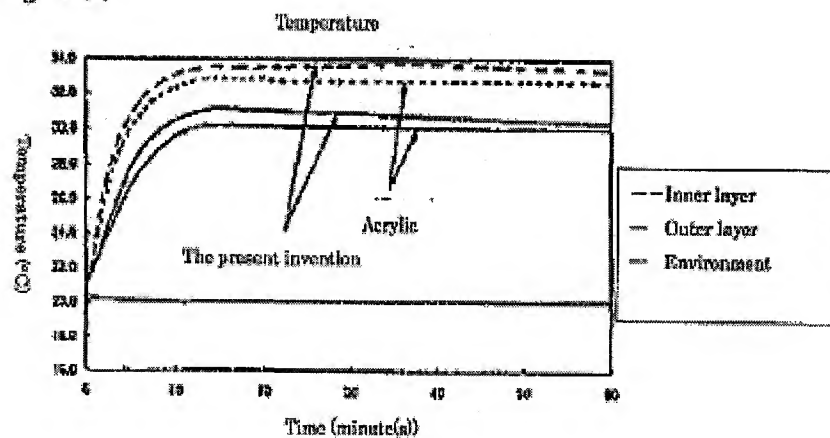


Fig. 7 (b)

